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Reactions and Interactions in Liquid Crystalline Media

by

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<p>This chapter discusses critically the most representative examples of reactions performed both in low molar mass and polymeric liquid crystals. Examples of reactions whose pathway is affected when they are performed in low molar mass liquid crystals, as well as reactions performed on polymeric liquid crystals whose phase behavior is affected whether the reaction takes place in the isotropic or anisotropic solution or melt are discussed. Separation and transport processes in which the interaction between solute and low molar mass or polymeric liquid crystalline solvent affects the overall process are also discussed. Organization, miscibility, phase diagrams and reactions of any kind including polymerization in low molar mass and polymeric liquid crystals is an interplay of molecular chemistry (i.e., the chemistry of the covalent bond) and supramolecular chemistry (i.e., the chemistry of intermolecular bonding through specific interactions).</p>			
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1. Introduction

Liquid crystals were discovered in 1888 by the Austrian botanist Reinitzer¹ who observed that cholesteryl benzoate exhibits two melting points. The first melting at 145.5 °C transforms the crystal phase into an anisotropic, turbid liquid which "melts" into an isotropic, clear liquid at 178.8 °C. This anisotropic liquid was first named by Lehmann in 1889 "flowing crystals", then "crystalline liquid" and finally "liquid crystal" in 1900.² The first synthetic nematic liquid crystals were prepared by Gattermann in 1890.³ The first smectic liquid crystals were synthesized by Vorländer in 1902.⁴

The fifty-eight discussion organized by the Faraday Society on the 24th and 25th of April, 1933 was devoted to "Liquid Crystals and Anisotropic Melts",⁵ thus recognizing the general scientific interest in the field of liquid crystals. The proceedings of this meeting are still providing a comprehensive entry to this field. In our opinion, the most valuable monographs describing the dependence between the molecular structure and the properties of thermotropic liquid crystals remain the book published by Gray in 1962 and his subsequent reviews.^{6a,b,c,d} The history of the entire field of liquid crystals was described by Kelker.^{7,8} A systematic description of the molecular structure-properties development during the first one hundred years of liquid crystal chemistry was published by Demus.⁹ Additional monographs which can introduce the reader to the field of both thermotropic and lyotropic liquid crystals¹⁰⁻¹³ and provide basic information also on its history,^{7,8,11} classification¹⁴ and identification of various mesomorphic textures,^{15,16} are available.

To our knowledge, the idea of performing chemical reactions in anisotropic liquids belongs to Svedberg who reported his first experimental data in 1916.¹⁷⁻²⁰ In his publications Svedberg showed that the rate of decomposition of picric acid, trinitroresorcinol and pyrogallol, increases slightly with increasing temperature when the reaction is performed in the nematic phase of *p*-azoxyphenetole, jumps at

the clearing point and continuous steeply upwards in the isotropic liquid. In addition, the reaction rate exhibits a distinct change when the nematic phase is under the increasing influence of a magnetic field. Regardless of the accuracy of these results, they suggest that an anisotropic phase can play the role of a "catalyst" in a certain reaction.

As early as 1922 Lehmann²¹ recognized that some of the properties exhibited by liquid crystals may have analogies to those of the living state. At the Faraday Discussions from 1933^{22,23} it was clearly recognized that the mobility and structural order of biological and synthetic liquid crystals furnish an ideal medium for catalytic action and that the living cell is actually a liquid crystal.

A significant citation from Bernal made at the Faraday Society meeting in 1933 is as follows:²³

"Rinne was not the first to see that liquid crystals had a bearing on biological problems, but I think that he had glimpsed at the fundamental rôle that they played, and understood the essential nature of the properties that enabled to do so.

The biologically important liquid crystals are plainly two or more component systems. At least one must be a substance tending to para-crystallinity and another will in general be water. This variable permeability of liquid crystals enables them to be as effective for chemical reactions as true liquids or gels as against the relative impenetrability of solid crystals. On the other hand, liquid crystals possess internal structure lacking in liquids, and directional properties not found in gels. These two properties have far-reaching consequences. In the first place, a liquid crystal in a cell through its own structure becomes a proto organ for mechanical or electrical activity, and when associated in specialized cells in higher animals gives rise to true organs, such as muscle and nerve. Secondly, and probably more fundamentally, the oriented molecules in liquid crystals furnish an ideal medium for catalytic action, particularly of the complex type needed to account

for growth and reproduction. Lastly, a liquid crystal has the possibility of its own structure, singular lines, rods and cones, etc. Such structures belong to the liquid crystal as a unit and not to its molecules which may be replaced by others without destroying them, and they persist in spite of the complete fluidity of the substance. These are just the properties to be required for a degree of organization between that of the continuous substance, liquid or crystalline solid and even the simplest living cell".

Today, it is well accepted that many of the low molar mass and polymeric biological derivatives exhibit liquid crystalline phases.²⁴⁻³⁵ Although the elucidation of the role of liquid crystalline phases in various biological processes is in an early stage of development, it should be quite instructive to recall the following statement: "*Liquid crystals stand between the isotropic liquid phase and the strongly organized state. Life stands between complete disorder, which is death and complete rigidity which is death again*".²⁴

Onsager in 1933³⁶ and Flory in 1956³⁷ predicted that rigid rod-like macromolecules should display liquid crystallinity. However, the first main chain thermotropic liquid crystalline polymer was reported in open literature only in 1975.³⁸ This publication is independent from the flexible spacer concept publication of deGennes³⁹ in the same year. However, patents on thermotropic main chain liquid crystalline polymers were published in 1973.⁴⁰ Publications dealing with the driving force behind the development of main chain thermotropic liquid crystalline polymers and various historical variants of these developments are available.⁴¹⁻⁴⁷

Although the field of thermotropic side chain liquid crystalline polymers is older than that of thermotropic main chain liquid crystalline polymers, systematic investigations in this field started only after Ringsdorf et al. introduced the spacer concept in 1978.^{48,49} Several monographs and review articles on side chain and main chain liquid crystalline polymers are available.⁵⁰⁻⁵⁷

Since the goal of this chapter is to discuss reactions and interactions which take place mainly in a thermotropic liquid crystalline phase, we will make a brief introduction to low molar mass and polymeric liquid crystals. For additional information on this topic the reader should consult the literature cited in this introduction.

1.1 A Brief Introduction to Low Molar Mass Liquid Crystals

A liquid crystalline or mesomorphic phase or mesophase refers to a state of matter in which the degree of order is between the almost perfect long-range positional and orientational order present in solid crystals and the statistical long-range disorder characteristic of isotropic or amorphous liquids and gases. Mesogens or mesogenic groups are compounds which under suitable conditions give rise to mesophases. They can be classified in non-amphiphilic (i.e. most frequently compounds exhibiting a rod-like or disc-like shape) and amphiphilic (i.e. compounds that contain within the same molecule lipophilic and hydrophilic groups which have the ability to dissolve in organic solvents and water respectively). Thermotropic mesophases are induced by a change in temperature, while lyotropic mesophases are induced by a solvent. Some mesogens can generate amphotropic mesophases, i.e. the liquid crystalline phase can be induced either by a change in temperature, by a solvent, or by both.^{59a} Other highly immiscible groups like perfluorinated and paraffinic, available within the structure of the same molecule also give rise to amphotropic mesophases.^{59b}

Depending on their thermodynamic stability with respect to the crystalline phase, thermotropic mesophases can be virtual (unstable with respect to the crystalline phase), monotropic (metastable with respect to the crystalline phase), or enantiotropic (stable with respect to the crystalline phase).^{60,61} Virtual mesophases exist only below the melting and crystallization temperature and therefore can not be observed. Monotropic mesophases can be observed only during cooling due to the

fact that the crystallization process is kinetically controlled and therefore is supercooled, while the liquid crystalline phase is thermodynamically controlled and is not supercooled. Enantiotropic mesophases can be observed both on heating and cooling. For the purpose of this chapter we are concerned only with enantiotropic liquid crystalline phases.

Thermotropic mesophases exhibited by rod-like or calamitic mesogens can be classified in uniaxial, biaxial, and chiral nematic (cholesteric), and a number of different smectic phases which form either an untilted layer (smectic A, s_A etc.) or a tilted layer (smectic C, s_C etc.) structure (Scheme 1). Characteristic for the nematic phase is a parallel orientation of the molecules with an axis that corresponds to the long axis of the mesogen. While uniaxial nematic phases (biaxial nematic⁶² phases are not of interest for this discussion) exhibit a one-dimensional degree of order, smectic phases can exhibit a two-dimensional (s_A , s_C exhibiting unstructured layer structures) or a three-dimensional (s_B , s_G , s_E , s_H exhibiting structured layer structures) order.¹⁶ Disc-like molecules exhibit various columnar or discotic mesophases which will not be discussed further here.^{63,64}

Upon increasing their concentration, amphiphilic mesogens generate isotropic, and then micellar solutions. At higher concentrations rod-like micells generate hexagonal mesophases while spherical micells generate cubic mesophases. Alternatively an isotropic solution of an amphiphilic molecule can assemble directly into a lamellar liquid crystalline phase (Table I).^{11,22,32,35,65,66}

1.2 Liquid Crystalline Polymers

Liquid crystalline polymers can be classified into main chain, side chain and combined (Scheme 2). This classification is based on the place of the polymer where the mesogen is inserted, i.e. within the main chain, as side groups, or both within the main chain and as side groups. More complex polymer architectures are also possible.^{9,59,67} The mesogen used in the construction of the liquid crystalline

polymer can be rod-like, disc-like or amphiphilic.^{9,59,67-69} In addition to linear polymer structures, cyclic,⁷⁰ branched and crosslinked⁷¹ architectures have also been synthesized. Therefore, liquid crystalline polymers display thermotropic and lyotropic mesophases which are similar to those exhibited by thermotropic and lyotropic low molar mass liquid crystals. In addition, rigid-rod like main chain non-amphiphilic polymers like poly(phenyleneterephthalamide) (Kevlar®),⁷² poly(*p*-phenylene-2,6-benzobisthiazole) and poly(*p*-phenylene-2,6-benzobisoxazole)⁷³ exhibit lyotropic nematic mesophases.

A characteristic of side chain liquid crystalline polymers is that their polymer backbone adopts a random-coil conformation only in solution and in isotropic melt. In a nematic phase the conformation of the polymer backbone is slightly disturbed. Depending on the flexibility of the polymer backbone, its conformation in the smectic phase is so highly distorted that it can even be confined to the smectic layer (in the case of polymers based on very flexible backbones) or it can cross the smectic layer (in the case of rigid backbones).⁷⁴⁻⁷⁶

1.3 Isomorphism of Liquid Crystals

The miscibility of various liquid crystalline low molar mass substances and polymers is of great importance when we consider reactions in a liquid crystalline phase. In the field of low molar mass liquid crystals, Arnold, Sackmann, and Demus have developed the miscibility rules⁷⁷⁻⁸⁰ which can be summarized as follows: If two liquid crystalline phases are miscible, they are isomorphic, and therefore belong to the same type of mesophase. However, the reverse is not true. The situation is more complicated for mixtures of liquid crystalline polymers with low molar mass liquid crystals and for mixtures of liquid crystalline polymers. Many times similar phases of liquid crystalline polymers and low molar mass liquid crystals are not miscible.⁸⁰⁻⁸³ The same is the case for similar phases of two

different liquid crystalline polymers.⁸⁴ For a general discussion on this topic see reference 84.

Mixtures of nematic liquid crystals with isotropic solute molecules varying in size and shape have been studied extensively over the past years both experimentally⁸⁵⁻⁸⁹ and theoretically.⁹⁰⁻⁹³ The addition of an isotropic solute to a liquid crystalline solvent decreases the nematic-isotropic transition temperature of the solvent and leads to a two phase region. This phase behavior is very sensitive to the shape of the solute and its molecular weight. Thus a change of the shape of the solute from elongated to more isotropic and an increase of its molecular weight, are both leading to a sharper decrease of the nematic-isotropic transition temperature. Flexible random-coil polymers are not miscible at all with low molar mass liquid crystals or with liquid crystalline polymers. For example, a smectic low molar mass liquid crystal could theoretically accommodate a random-coil polymer only between the smectic layers.⁹⁴

All this discussion should be carefully considered in attempts to interpret the possible role of a liquid crystalline solvent on the course of a chemical reaction. A liquid crystalline solvent can influence such a reaction in an interpretable way only when the reagents, the liquid crystalline solvent and the reaction products are all miscible. Reactions performed in microphase separated systems are much more difficult to be explained since they are not affected at all by the liquid crystalline solvent or are affected only at the interface. When the microphase separation is conversion dependent, as it is the case in most reactions, the problem is almost impossible to interpret.

1.4 Some Considerations on the Reactivity of a Solute in an Anisotropic Phase

Weiss⁹⁵ reviewed the model which explains how isotropic molecules dissolve and react in anisotropic solvents or media. In order to maintain the energy

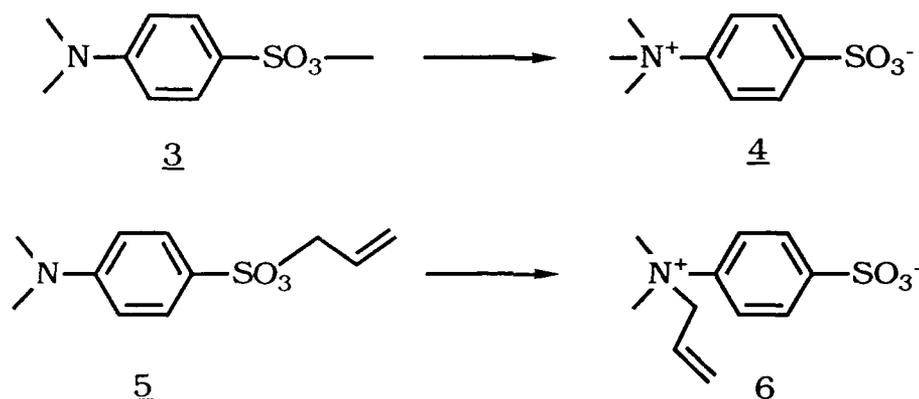
of the solute-solvent system low, the solute molecules will disturb the organization of the solvent as little as possible (Scheme 3). This means for example, that a rod-shaped molecule dissolved in a nematic solvent will align along the director of the system and in a smectic solvent along the director or in between the layers. The degree of disturbance of the system is determined partly by the difference in size and structure between the solute and solvent. Electronic factors, such as dipole-dipole, electron donor-acceptor, enthalpic and other interactions are favoring the interaction between solute and solvent molecules and therefore, affect the structure of the transition states that are formed. That is, the transition state that least disturbs the organization of the solvent, will be favored. In this way, the products formed in a reaction can be affected by the nature of the liquid crystalline solvent. However, not only the order of the solvent is important but also how easy it is to distort the liquid crystalline matrix during the reaction. According to this discussion, miscible isotropic solute-anisotropic solvent systems can influence the reaction pathway in a different way than a miscible isotropic solute-isotropic solvent system. When the system solute-solvent is microphase separated the reaction pathway is independent of the solvent nature regardless whether it is isotropic or anisotropic. Since miscibility is both enthalpically and entropically controlled, the ability of a pair of compounds to generate a miscible system decreases with the increase of their molecular weight and the increase in the dissimilarity of their molecular shape.

In the following subchapters we will discuss critically representative examples of reactions performed both in low molar mass liquid crystals as well as in polymeric liquid crystals. A recent review describes reactions in low molar mass liquid crystals.⁹⁵ Therefore, we will discuss only selected examples of reactions whose pathway is affected when they are performed in low molar mass liquid crystals, since they should be considered as representative examples for similar experiments performed with polymeric liquid crystals. Various reactions which are

performed on polymeric liquid crystals in their isotropic solution or melt and affect their phase behavior will be also discussed. Separation and transport processes in which the interaction between the solute and the low molar mass or polymeric liquid crystalline solvent affects the overall process will be also discussed.

2.2. Quaternizations

Samori and co-workers have studied⁹⁷⁻¹⁰⁰ the quaternization reactions of methyl and allyl p-(dimethylamino)benzenesulfonates (3 and 5) in a smectic B solvent.



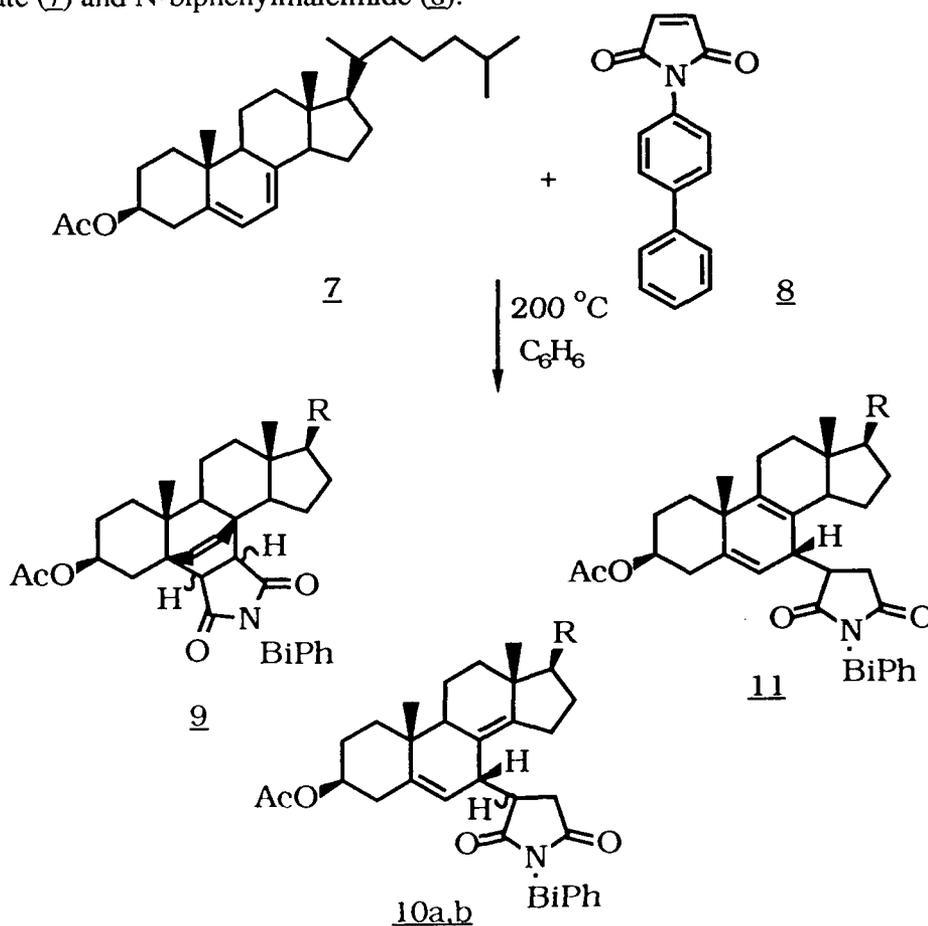
3 is known to rearrange to p-(trimethylammonium)benzenesulfonate (4) in the crystalline state through an intramolecular migration of the methyl group.¹⁰¹ The necessity of an ordered stacking of the molecules 3 for the rearrangement to take place, is demonstrated by the rapid decrease in the rate of rearrangement when the reaction is performed above the melting point of 3. Also, in solution no rearrangement takes place and 3 is completely stable. 5, on the other hand, does not rearrange to its corresponding sulfonate 6 neither in solution nor in the crystalline state. Most likely due to the increased bulkiness of the rearranging group of 5 compared to that of 3 the stacking of the molecules 5 is changed and the reaction can not take place.⁹⁸

Liquid crystalline solvents exhibiting sB phases, were found to support the rearrangement of both 3 and 5, but the nematic and isotropic phases of the liquid crystalline solvents did not. Since no anomalous dependence of the rate of rearrangement on the temperature below and above the melting of 3 was found, it was concluded that the observed effect was not due to local crystallization or solute aggregation. Another interesting effect was found on changing the concentration of

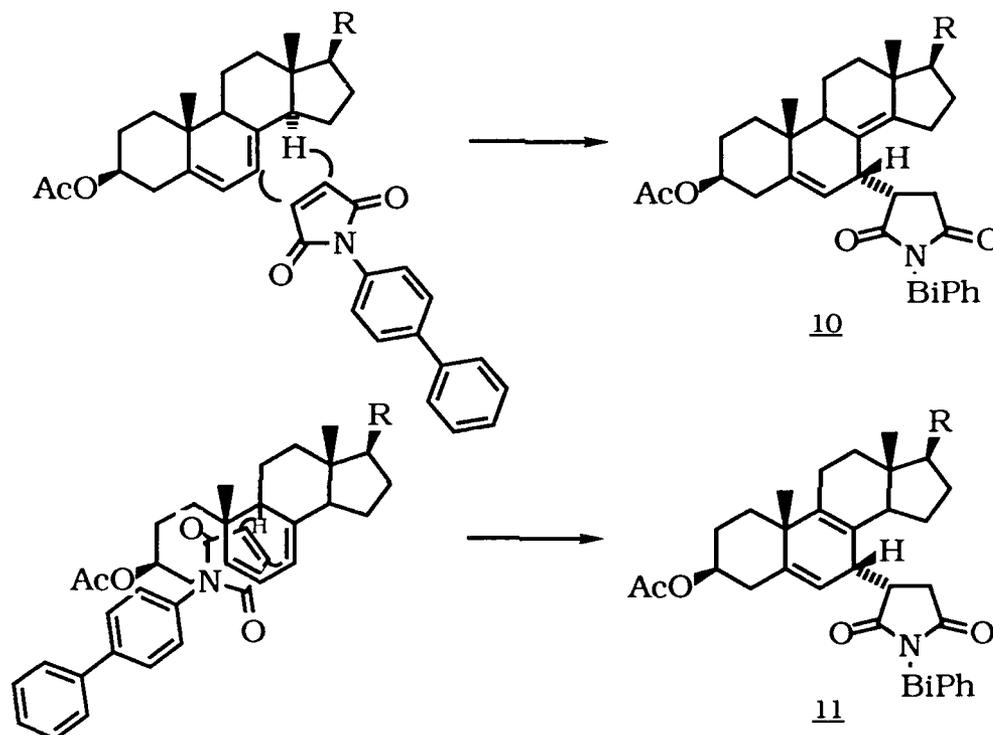
3 in the sB solvent above about 6.8×10^{-2} M. The reaction rate was lowered showing that the ordering imposed on the solute by the sB solvent gradually is disturbed when the concentration of solute becomes too high. The fact that the high order of the reacting molecules supposedly outweighs the high concentration also demonstrates that the possibility of performing the rearrangement in sB solvents should be due to crystallization. The authors concluded that the orientation of solute molecules in the sB solvent affected the free energy of activation of the reaction and thus made the rearrangement possible.

2.3. Cycloadditions

Leigh and Mitchell¹⁰² investigated the effect of molecular ordering on the course of ene and Diels-Alder cycloadditions between cholesta-5,7-dien-3 β -yl acetate (7) and N-biphenylmaleimide (8).



These reactions were carried out in the isotropic, smectic and cholesteric phases of liquid crystalline solvents as well as in benzene (Table II). In addition, formation of the ene product 11 was favored over the Diels-Alder adduct 9 and the other enes 10a,b, when the reactions were carried out in the liquid crystalline phase of the solvents. This was explained on the basis of different transition states for the products 10 and 11.



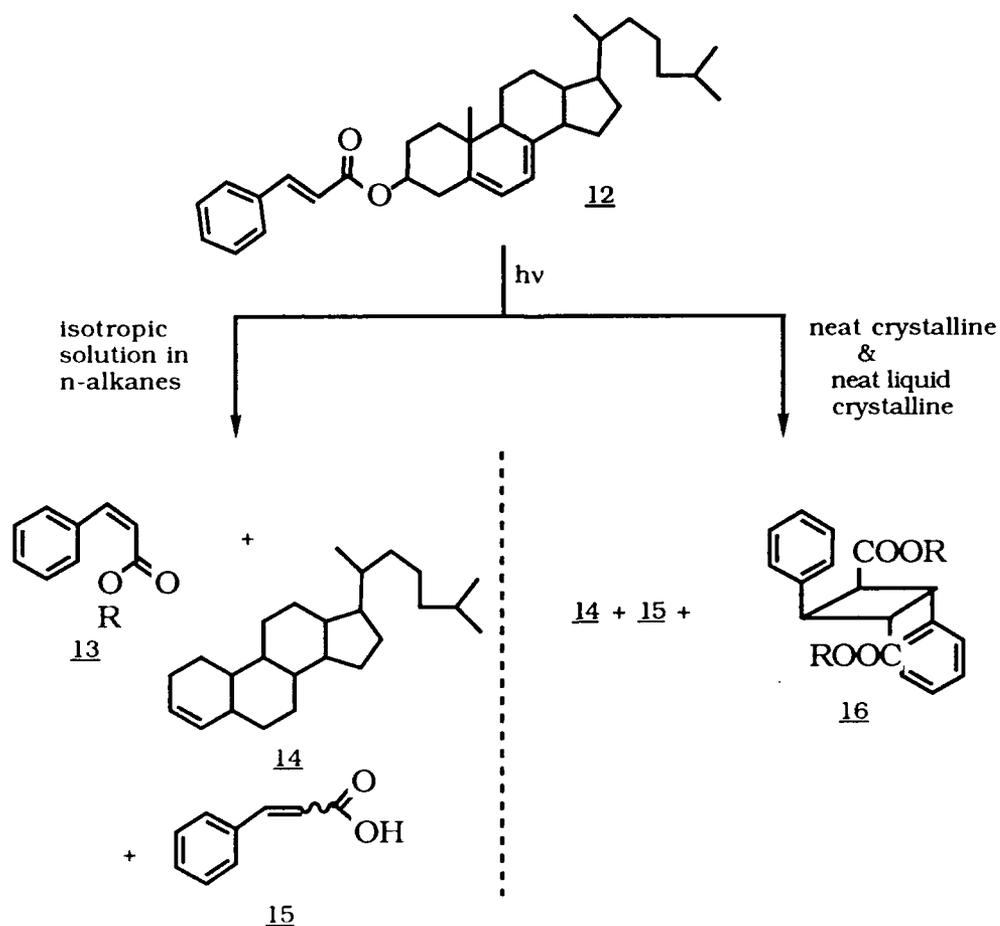
Formation of 11 requires a transition state in which the long axes of the reactant molecules are parallel to one another, while in the formation of 9 and 10a,b the reactant molecules are oriented in a perpendicular manner. Clearly the transition state in which the molecules are oriented in a parallel fashion will be favored in a surrounding of oriented molecules.

The effect on the reaction by increasing the order of the liquid crystalline phase of the solvent from cholesteric to s_B was rather limited. One would expect that the much higher order of the s_B mesophase should favor formation of 11 to a much higher extent than what was the case. The authors assigned this to the better

resemblance in structure between 7 and the cholesteric solvents than between 7 and the smectic solvent. In the smectic solvent the local order will be distorted, and thus will rule out the possibility of an increased orientation.

2.4. Photodimerizations

The photodimerization of 5 α -cholestan-3 β -yl trans-cinnamate (12) was studied by Ramesh and Weiss.¹⁰³ The isotropic solutions of 12 in n-hexane and hexadecane led to the following photoproducts: the cis-cinnamate (13) which results from the isomerization of 12, the cholestene (14) and the cis- and trans-isomers of cinnamic acid (15) which were formed from the cleavage of the ester groups of 12.

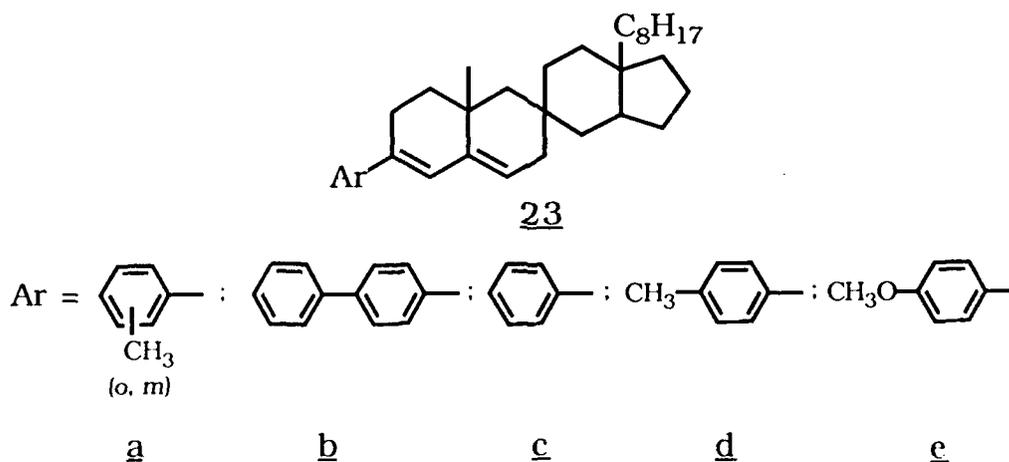


When the cinnamates were irradiated, two groups of dimers were formed, the α -truxillates (20) and the δ -truxinates (21). The former requires that a reaction should take place between overlapping cinnamoyl groups of molecules from adjacent layers (head-to-tail arrangement), while the latter is the result of dimerization taking place within a layer (head-to-head arrangement) (Figure 1).

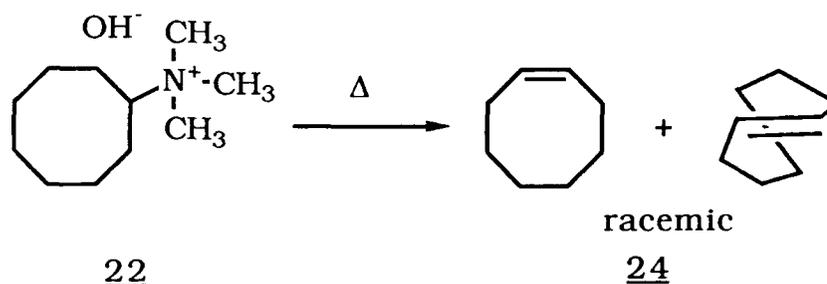
As can be seen from Table IV, the ratio of head-to-tail/head-to-head was significantly larger in the crystalline and s_B phases of butyl stearate than in the isotropic phase. Apparently, the ordered phases strongly promote the head-to-tail arrangement. This type of arrangement should also be supported, if taking into account the dipoles in the cinnamoyl groups. Further, the fact that the most soluble of the cinnamates in butyl stearate was 17, the longest one, and the least soluble 19 the shortest one, also supports the interdigitation theory. Two molecules of 17 with their cinnamoyl groups overlapping will have a length of approximately the width of two butyl stearate layers, and will in this way disturb the layers least.

2.5. Asymmetric Inductions

Optically active trans-cyclooctene was obtained by Hofmann elimination of trimethyl(cyclooctylammonium) hydroxide (22) in 3-aryl-substituted-3,5-cholestadienes (23a,b,c,d,e).¹⁰⁵



Depending on the type of liquid crystalline solvent, temperature and solute concentration, enantiomeric excesses obtained in the cholesteric solvent varied between 1 and 7.2 %. In the isotropic phase or in a nematic phase twisted by a small amount of a cholesteric molecule, racemic trans-cyclooctene (24) is produced.



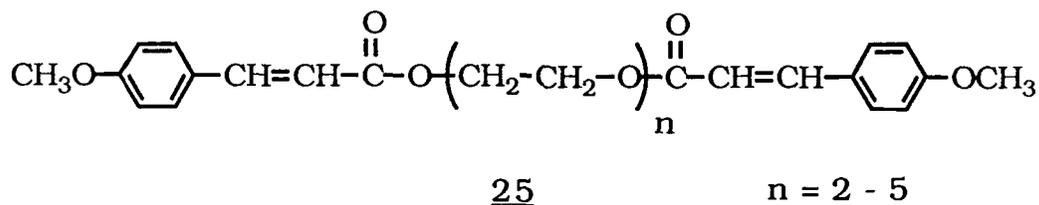
Enantiomeric equilibration of trans-cyclooctene in 3-aryl-substituted-3,5-cholestadienes (23a,b,c,d,e) afforded enantiomeric excesses of 1 to 1.9 % depending on the structure. However, in cholesterol esters, e.g. cholesteryl p-nitrobenzoate and cholesteryl benzoate, no asymmetric induction was achieved. These results were interpreted in terms of solute-solvent interactions enhanced by the local ordering of the mesophase.

Solladie and Gottarelli¹⁰⁶ used the ability of the nematic liquid crystals to be converted into cholesteric liquid crystals, when mixed with optically active materials, to determine the absolute configurations and the conformational analysis of biaryls. The helicity of the aryl compounds was assigned to be the main factor determining their twisting power in nematics.

2.6. Photoreaction of Cholesteryl Cinnamates

The photo-reaction of cholesteryl trans-cinnamate was studied in KBr matrix in the solid, liquid crystalline and isotropic states, and in solution in n-hexane.¹⁰⁷ The slowest isomerization rate was observed in the solid state and the fastest in the liquid crystalline state. The isotropic state gave an intermediary rate. It was concluded that ordering together with mobility determines the rate and the course of the reaction.

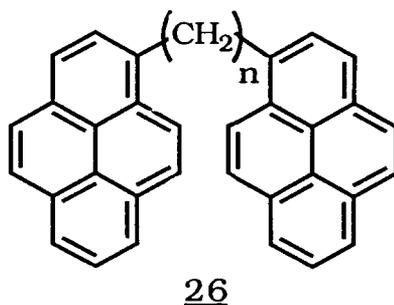
Twin dimers containing 4-methoxycinnamic acid moieties at both ends of various lengths of ethylene glycol spacers (25) were irradiated with UV light in their liquid crystalline state.¹⁰⁸



The liquid crystalline phase could not be assigned. The photoreactivity for $n=2$ and 3 increased in the order of crystalline < liquid crystalline < isotropic and for $n=4$ and 5 in the order of isotropic < liquid crystalline < crystalline. This result was attributed to different spatial orientation of the mesogenic chromophores. It was found that the morphology of the system affected the photoreactivity and that the head-to-head photodimer was predominantly formed.

2.7. Excimer Formation

The possibility for a hydrocarbon chain to be oriented in liquid crystalline media was studied by Weiss and co-workers.^{109,110} They investigated the rate at which α,ω -bis(1-pyrenyl)alkanes (26) form intramolecular excimers in the smectic, nematic, cholesteric, and isotropic phases of some liquid crystalline compounds. The excimer formation is readily followed by fluorescence spectroscopy since the monomer and excimer emissions are well separated.



$$n = 3, 5-7, 9-11, 13, 22$$

The activation energies for intramolecular excimer formation were found to be highly chain length dependent in anisotropic media, but not in isotropic media. In anisotropic media it increased with increasing length of the chain, whereas in isotropic media it leveled off to a constant value. The authors concluded that both the solvent order and solvent-solute interactions affected the excimer formation, i.e. the ring closure.

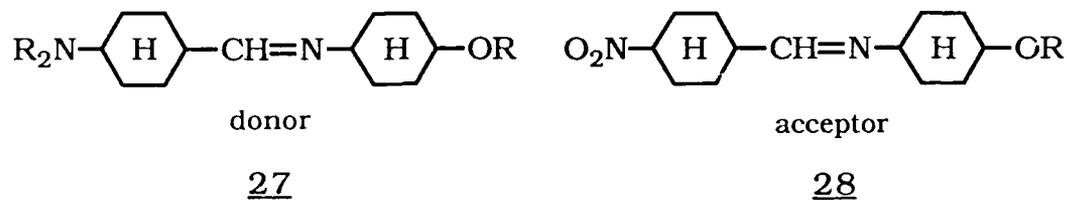
Ikeda et al.¹¹¹ studied the excimer formation of 4-n-pentyl-4'-cyanobiphenyl in the neat phase by steady-state and time resolved fluorescence spectroscopy. The excimer was found to be formed with high efficiency in the nematic phase. In the isotropic phase the formation was found to be less effective. An abrupt decrease in excimer formation efficiency was observed near the nematic-isotropic transition. They assigned the higher efficiency in the nematic phase to the orientation of the chromophores. In the nematic phase the chromophores are aligned parallel to each other which enables them to obtain face-to-face configuration (which is essential for excimer formation).

2.8. Electron Donor-Acceptor (EDA) complexes

Doping of low molar mass discotic liquid crystals with aluminum trichloride produced one-dimensional conductors.¹¹²

Addition of chiral dopants to nematic phases gives cholesteric phases¹¹³ and in the same way the sC phase is transformed into a chiral smectic C (sC*) phase.¹¹⁴

Liquid crystal compounds were generated from non-mesogenic (but potentially mesogenic) compounds by formation of donor-acceptor complexes between the compounds 27 and 28.^{115,116}

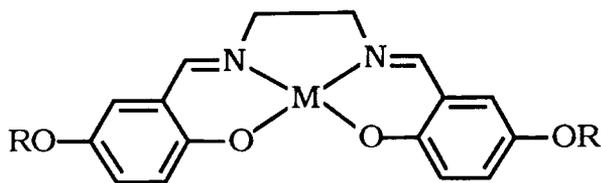


The nematic-isotropic transition was increased and the crystalline-nematic transition decreased, i.e. a broadening of the nematic temperature range was achieved, due to donor-acceptor interaction, when 4-aminobiphenyl was added to 4-cyano-4'-pentylbiphenyl.¹¹⁷

2.9. Transition Metal Complexes

Complexation of pro-mesogenic compounds with various metals leads to mesomorphic metal complexes. At the same time, complexes of various mesogens leads to compounds exhibiting new liquid crystalline phases. An excellent recent review on this topic was published.^{118a} Few examples are presented below.

Paschke et al.^{118b} have studied disalicylidene-ethylenediamine complexes of Ni(II) (29) and Cu(II) (30).



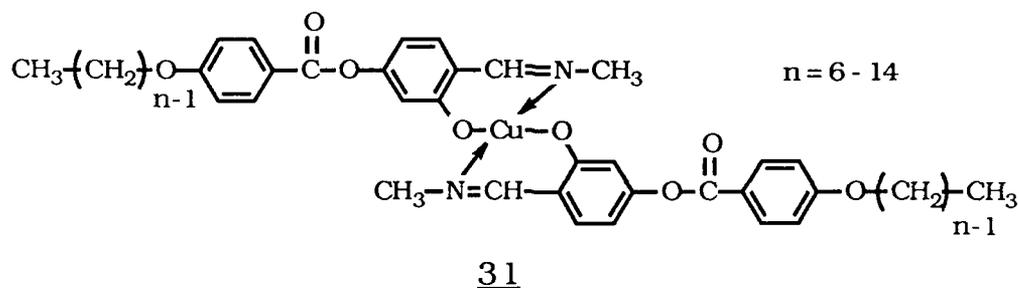
29 : M = Ni

30 : M = Cu

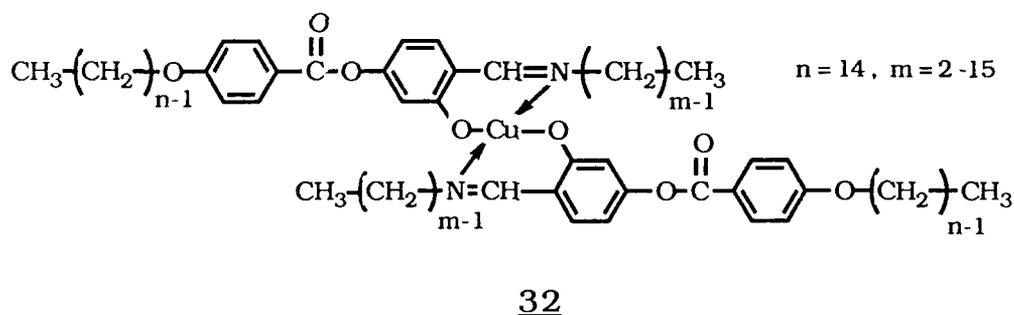
R = C_nH_{2n+1}

These complexes exhibited calamitic s_A phases. The width of the mesophase was larger for Ni(II) (35-115 °C) than for Cu(II) (7-26 °C).

A homologous series of copper organometallic complexes (**31**) were synthesized by Sirigu et al.¹¹⁹



These compounds showed nematic and s_C mesomorphism. The width of the mesophase decreased slightly with increasing the length of the alkoxy substituents. The same authors also investigated a second, similar system.¹²⁰



With one exception, complexes **32** were all mesogenic, exhibiting either nematic, smectic or both nematic and smectic mesophases.

2.10. Diffusion

Diffusion in thermotropic liquid crystals has been very thoroughly reviewed by Krüger.¹²¹ He states that diffusion is anisotropic in most cases. Self-diffusion in nematic mesophases is always faster parallel than perpendicular to the director of the molecule. However, the activation energy is approximately the same. The

diffusion of solutes in a nematic solvent shows the same behavior, though with less anisotropy in disordered smectic phases, i.e. s_A and s_C . The self-diffusion coefficients exhibit about the same value and instead the activation energies are anisotropic with $E_{\parallel} > E_{\perp}$. For the activation energies of solute diffusion, this effect is more pronounced and the perpendicular diffusion is also much larger than the parallel one. In ordered smectic mesophases like s_B and s_E , the self-diffusion is faster in the perpendicular direction, however, like in nematic mesophases, the activation energies are about the same.

2.11. Hydrolysis

A number of 4-substituted benzylidene t-butyl-amine N-oxides were hydrolyzed in cationic lamellar liquid crystalline media¹²² consisting of aqueous dodecylammonium chloride or a mixed system of dodecylammonium chloride and didodecyltrimethylammonium chloride. The rate constants of the aqueous acid hydrolysis decreased as the electron-releasing effect increased and they were linear when plotted against σ^+ -substituent constants. It was concluded that the rate of hydrolysis in the lamellar liquid crystalline system was dependent upon:

- i) partitioning of the substrate between the aqueous and hydrocarbon regions
- ii) the electrostatic effect of the surfactant aggregate upon intermediates
- iii) the morphology of the system.

Ramesh and Labes¹²³⁻¹²⁷ have studied chemical reactions in aqueous lyotropic nematic media. Both unimolecular, e.g. photoisomerization of a merocyanine to a spiropyran in anionic surfactants, and bimolecular, e.g. catalyzed ester and phosphinate ester hydrolysis in a cationic surfactant have been investigated. Very large changes in reaction rates have been observed in the lamellar, cylindrical and spherical phases. The isomerization of a merocyanine to an indolinospiropyran was studied in the nematic lyophases of potassium laurate, myristyl trimethylammonium bromide or sodium decylsulfate with 1-decanol and

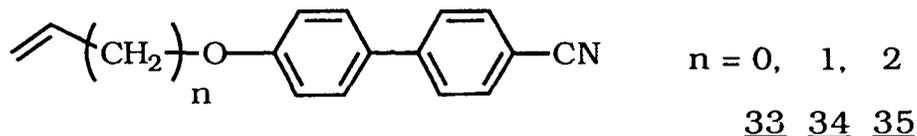
water. A strong retardation of the rate of isomerization was observed in the lamellar phase. By the use of polarized absorption spectroscopy it was possible to determine the order parameter for the spiropyran and the merocyanine in the lamellar and the cylindrical phases. The much higher order of the merocyanine compared to the spiropyran, combined with the decrease of rate in the lamellar phase, indicates that the bilayer structure of the lamellar phase restricts the spiro ring formation more than the cylindrical structure. This was attributed to the "trapping" of the merocyanine molecules within the bilayer matrix. Also the difference in internal viscosity between the different phases, due to variations in the segmental motions of the surfactants in the proximity of the merocyanine molecules, probably affects the rate of isomerization.

The bimolecular reactions studied were the cleavage of *p*-nitrophenyl laurate¹²⁴ and *p*-nitrophenylethyl(phenyl)phosphinate¹²⁷ catalyzed by *o*-iodosobenzoic acid in the nematic, lamellar and cylindrical lyophase of myristyl trimethylammonium bromide/water/ammonium bromide/1-decanol. For the former case, the rate of ester cleavage was found to be 5 times higher in the cylindrical phase than in the lamellar phase. For the latter case, a more than 3 orders of magnitude difference was found. Based on infrared measurements, the authors concluded that since in the lamellar phase the solute is solubilized in the hydrocarbon region, it will be protected against ester cleavage. The cylindrical and spherical phases do not offer this shielding since the solute is located closer to the aqueous outer phase, and consequently the rate of ester hydrolysis is higher.

3.1 Polymerization in Thermotropic Liquid Crystalline Media

3.1.1. Thermally Initiated Bulk Polymerizations

Dubois et al.¹²⁸ investigated the thermally induced bulk polymerization of the monomers 33-35 in their nematic state. It is interesting to mention that alkenes do not polymerize thermally in an isotropic phase.



The plot of conversion in weight % versus time for 3 different temperatures within the nematic mesophase of 33 ($n=0$) were found to be linear up to 80 % conversion. This led the authors to conclude that monomer and polymer are completely miscible and no phase segregation occurs. The polymer was found to be insoluble in all common solvents and did not exhibit any thermal transitions up to 260 °C. Optical polarized microscopy of a thin film of the polymer revealed a "disordered mesophase".

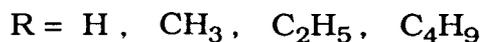
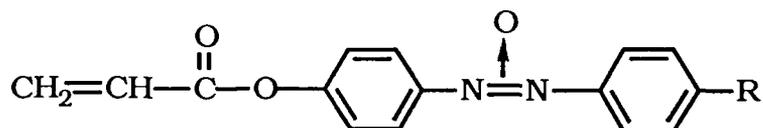
In a survey, Cser et al.¹²⁹ investigated the polymerization in the mesomorphic state and considered it by analogy with solid state polymerization. According to these authors, the polymer formed in the reaction interacts with the initial monomer phase giving rise to a new thermodynamic system. The reaction can be either a homogeneous or a heterogeneous topochemical reaction, the homogeneity or heterogeneity being dependent only on whether the polymer formed is isomorphous with the monomer or not. Homogeneous topochemical polymerization can be expected in smectic mesophases where the functional groups of the layer formed by the parallel chains are located in one plane. The situation is completely different in the cholesteric or nematic states. These states do not seem to favor topochemical processes, and therefore, an isomorphism cannot be expected

either. The rates of polymerizations are usually lower, and the activation energies higher than those in the isotropic state measured or extrapolated to the same temperature.

Barrall et al.¹³⁰ in a review of polymerization in thermotropic liquid crystalline media comment on two potential problems. One is phase separation during polymerization in certain systems as identified by Amerik et al.^{131a} and Blumstein et al.^{131b,134} This phase separation may explain all of the unusual results reported by these authors. The second one is the question of whether the polymerization is taking place homogeneously since as the reaction proceeds in the mesophase, the mesomorphic to isotropic transition temperature is seriously depressed.

Blumstein et al.^{131b} have polymerized p-methacryloyloxybenzoic acid both in nematic p-n-heptyloxybenzoic acid, smectic p-n-cetyloxybenzoic acid and in isotropic solvents (DMF). The solubility of the monomer in the anisotropic solvents was inferred by constructing phase diagrams of the saturated model p-propionoxybenzoic acid and the anisotropic solvents. The solubility of the monomer did not exceed 0.2 mole fraction of monomer in smectic p-n-cetyloxybenzoic acid and 0.3 mole fraction of monomer in nematic p-n-heptyloxybenzoic acid. The molecular weights of polymers prepared in the anisotropic solvents were much higher than those prepared in DMF. At the same time the molecular weight distributions of the former polymers were somewhat broader than those of the latter. For polymers prepared in the nematic solvent p-n-heptyloxybenzoic acid at monomer concentrations between 0.2 to 0.66 mole fraction neither the molecular weights nor the molecular weight distributions appeared to be significantly influenced by the presence of excess monomer crystal.

Cser et al.¹³² have polymerized azoxyacrylate monomers (36-39) in the nematic state and in solution.



The phase diagram of the p-methyl-p'-acryloyloxyazobenzene monomer (37)/polymer system was determined using a combination of differential scanning calorimetry, X-ray diffraction, thermomechanical analysis and optical polarization microscopy. The monomer and polymer were found to form a complete miscible series both in the nematic and in the isotropic state. Based on this phase diagram, the authors concluded that a reasonable interpretation can be given for the observation of the identical structure of the polymer formed either in the liquid or in the nematic state.

A good general discussion about older literature data on polymerizations in liquid crystalline media is presented in reference 133. A "good" system for the investigation of the effects of liquid crystalline media on polymerization kinetics is N-(p-cyanobenzylidene)-p-aminostyrene which produces by radical polymerization a polymer soluble in the nematic mesophase of its parent monomer. The activation energy of the polymerization in both the nematic and the isotropic state was the same i.e., 107.5 kJ/mole. The resulted polymer did not show any mesomorphic transitions.

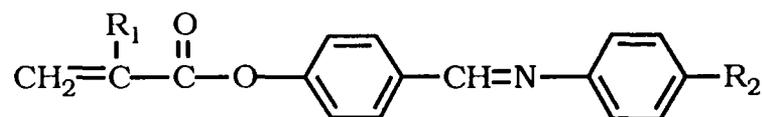
Blumstein et al.¹³⁴ have investigated the oriented polymer growth in thermotropic mesophases. They have considered that "locking in of mesomorphic superstructures through polymerization is analogous to locking in of molecular orientation through cooling". However, according to these authors, so far the difference in supramolecular organization between the polymer prepared in isotropic

and mesomorphic media is unclear. This behavior is determined by the interplay of the following three factors:

- a) influence of the organization of the initial monomeric matrix (topotactical control)
- b) strong interaction between side groups of the polymer, i.e. the polymer's intrinsic tendency to organize
- c) possible influence of the matrix on the configuration of the polymer (topochemical control) which would in turn influence the supermolecular organization

The polymerization of N-p-methacryloyloxybenzylidene-p-aminobenzoic acid in bulk without initiator and in isotropic solution in DMF with peroxide initiator produced nematic polymers. The polymerization of N-p-butoxybenzylidene-p-aminostyrene in bulk at the onset of the crystalline to nematic transition and in the nematic mesophase was carried out with radical initiators. The authors claimed that the mesophase of the monomer gets "frozen in" during polymerization, while the mesophase of the polymer "fades away" on heating because the polymer decomposes before it becomes isotropic. Polymerization of p-methacryloxybenzoic acid in p-heptyloxybenzoic acid (a nematic solution is formed) gave a birefringent polymer, whereas bulk polymerization of p-methacryloxybenzoic acid or solution polymerization of p-methacryloxybenzoic acid in a non liquid crystalline solvent o-ethoxybenzoic acid or p-methacryloxybenzoic acid and p-heptyloxybenzoic acid in isotropic solution did not produce liquid crystalline polymers.

Perplies et al.¹³⁵ have polymerized anionically the acrylates 40 and methacrylates 41 both in solution and in bulk.



40 $\text{R}_1 = \text{H}, \quad \text{R}_2 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OC}_4\text{H}_9$

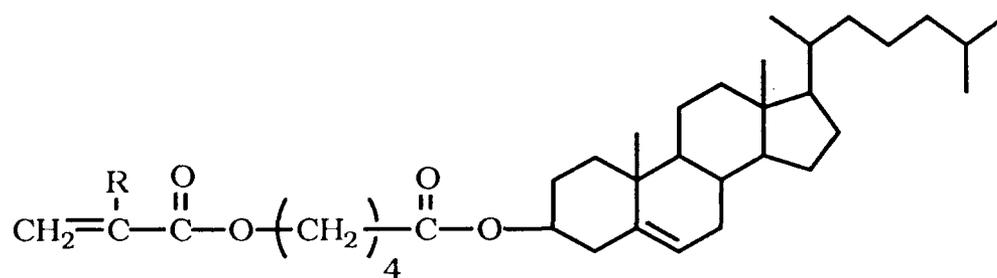
41 $\text{R}_1 = \text{CH}_3, \quad \text{R}_2 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OC}_4\text{H}_9$

A comparison of the overall polymerization rate in the anisotropic and in the isotropic melt showed that the rate increased suddenly when the melt became isotropic. The authors explained this result to be due to the lower mobility in the anisotropic state. The structure of the polymers depended on the polymerization conditions. The polymers prepared in solution at 20 °C were amorphous whereas the polymers prepared in the nematic phase had similar structure with those prepared in solution at -78 °C with subsequent annealing. The authors considered the possibility of monomer aggregation in solution at low temperatures.

Mixtures of p-methyl-p'-acryloyloxyazobenzene and cholesteryl vinylsuccinate were polymerized in the nematic and cholesteric mesophases at 82 °C using benzoyl peroxide as initiator.¹³⁶ The rate of copolymerization in the two phases went through a maximum as a function of the composition and the rate of polymerization in the mesophase was in every case lower than that in the isotropic phase. Since the two states were realized at the same temperature (by the addition of dioxane to provide isotropic state), they attributed the difference to structural reasons i.e., the restricted motion of the functional group in the mesophase.

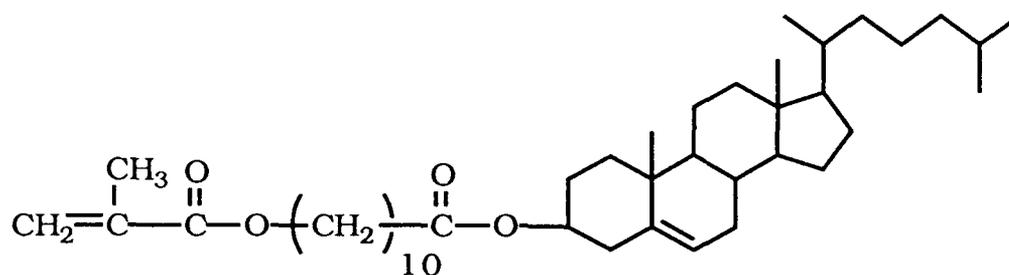
3.1.2. Photochemically Initiated Bulk Polymerizations

Hoyle et al.¹³⁷ have investigated the photoinitiated bulk polymerization of 42.



The polymerization rate is highest in the cholesteric state as compared to both the isotropic and the two crystalline states of the monomer. The rate of polymerizations in the liquid crystalline and isotropic states are higher than in the crystalline states due to restricted mobility in the latter. The rate of polymerization in the liquid crystalline state is higher than that in the isotropic state due to the higher degree of ordering in the former.

Hoyle et al.¹³⁸ have investigated the photopolymerization kinetics of monomer 43 in the crystalline, smectic, cholesteric and isotropic phase.

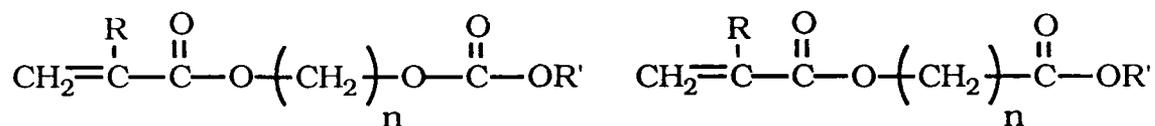


43

The rate of polymerization was characterized by studying two parameters; the maximum rate of heat evolution (H_{\max}) and the time (T_{\max}) required to reach H_{\max} (Table V). The rate of polymerization was found to be dependent on the phase of the monomer. Polymerization in either mesomorphic phases was very rapid in comparison to the rate in the isotropic or crystalline phases. Additionally, the rate in the cholesteric phase was found to be somewhat higher than in the smectic phase. According to the authors, the cholesteric phase seems to provide the optimum balance between monomer order and translational mobility resulting in a maximum polymerization rate.

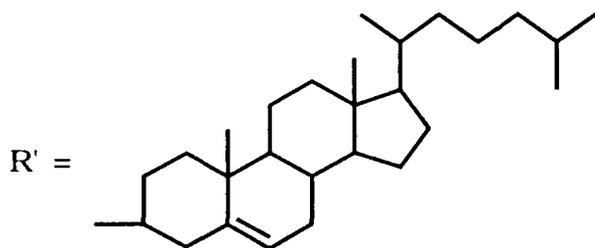
Cholesteric acrylate and methacrylate carbonates (44) and esters (45) were photopolymerized in the cholesteric state¹³⁹ by UV irradiation for 30 seconds to 70-80 % conversion to polymer. The cholesteric mesophases of the monomers were "frozen in" upon polymerization to cholesteric planar textures. The optical

properties of the films thus produced were stable for a year under ambient conditions. The planar cholesteric phase dissipated irreversibly upon heating above the cholesteric-isotropic transition temperature. The author suggested that the cholesteric phase is metastable and heating above the isotropization temperature allows the polymer to reorganize to a more ordered smectic phase upon cooling.

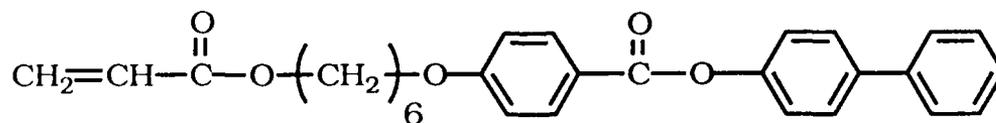
4445

<u>n</u>	<u>R</u>
6	CH ₃
2	CH ₃
6	H
2	H

<u>n</u>	<u>R</u>
10	CH ₃
5	CH ₃
3	CH ₃
10	H
5	H
3	H

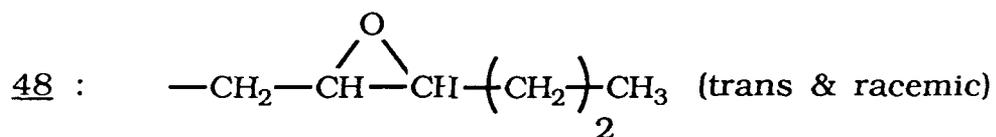
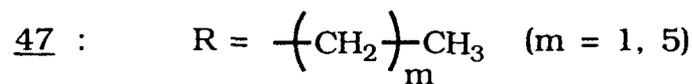
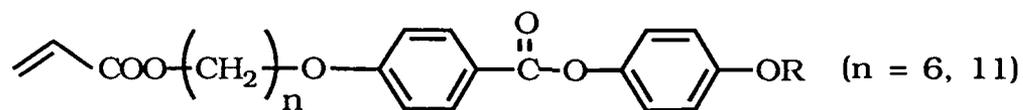


Photoinitiated polymerization of 46 in its oriented liquid crystalline state has been investigated.¹⁴⁰

46

Both the birefringence and the liquid crystalline transition temperatures increased upon copolymerization, indicating that the orientation was maintained during polymerization. The course of the polymerization depended on the phase of the monomer.¹⁴¹ If the monomer phase was a monotropic smectic A or a monotropic nematic phase, crystallization took place during the copolymerization and this affected the polymerization rate and conversion. However, in the thermodynamically stable i.e. enantiotropic nematic phase, the polymerization was fast and complete. During the polymerization, the transition from the nematic phase of the monomer to the smectic phase of the polymer took place and this process caused a microphase separation of the reaction mixture (Figure 2). This phase separation was also attributed to be responsible for the high polymerization rate. The segregated polymer forms a gel with a higher conversion and the smectic configuration in this gel was believed to contribute to the suppression of termination. The early gelation due to phase separation was believed to have the same effect as the Trommsdorff effect in diacrylates. *No effect of the initial phase of the monomer on the polymerization kinetics was observed at the onset of polymerization.* Polymerizations carried out in the isotropic phase of the monomer were markedly slower. One explanation was that early segregation of polymer (sample turbid in the microscope) shielded the UV light. Another "more direct cause" was that multi-domains were formed at the moment of the transition from isotropic to liquid crystalline phase and these domains could not rearrange themselves in the medium due to the rapidly increasing viscosity. The monomers were oriented prior to polymerization by interaction with a thin rubbed polyimide coating. It was shown that the macroscopic orientation of the monomer was preserved during the polymerization, resulting in highly ordered polymers.

Solid-state polymerization of monofunctional acryloyl monomers having different phenyl benzoates as mesogens (47, 48) was performed using a low-energy electron beam.¹⁴²



The polymerizations were performed on cast films that had been heated to 110 °C and subsequently annealed at room temperature. The monomers exhibited nematic, cholesteric, and smectic mesophases. The epoxy containing monomers (48) gave insoluble crosslinked polymers that exhibited nematic and smectic mesophases.

3.1.3. Copolymerization in Liquid Crystalline Media

A review paper on copolymerization in liquid crystalline media was published by Hardy et al.¹⁴³ These authors have recognized that the polymerization reactions are homogeneous only if the parent monomer and the polymer formed display identical mesophases. The effect of the liquid crystalline phase on the reaction parameters and on the structure of the resulted polymer can be therefore investigated unequivocally only when the polymer is completely miscible with the parent monomer. Additionally, for copolymerization reactions, a homogeneous reaction can be expected only under homogeneous phase conditions, that is, only when both comonomers have the same mesomorphic state and the ability to form homogeneous solution is not inhibited by chemical structure differences.

The reactivity ratios are not determined only by the structure of the terminal unit of the growing chain but depend much more on the interaction of the macroradical with the monomeric molecules from its surrounding. Both the

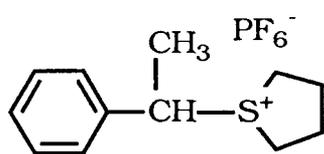
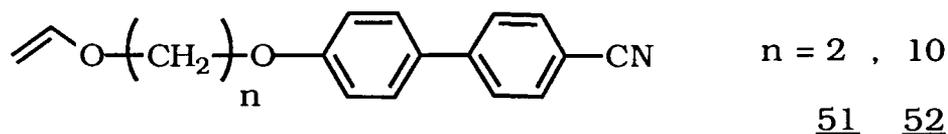
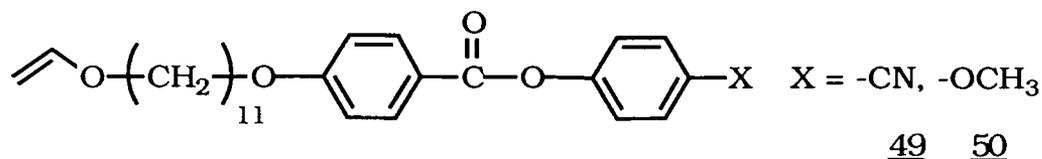
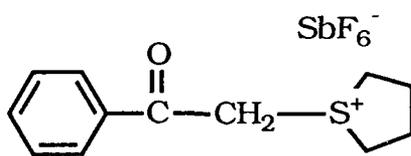
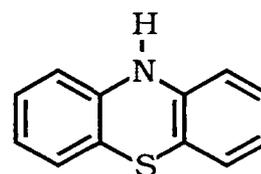
chemical and the physical structures of the copolymer built up from potentially mesogenic vinyl monomers are more dependent on topochemical than on purely chemical conditions. Copolymerization experiments were also carried out,¹⁴⁴ in isotropic solutions. In the nematic state, rotation of the molecules about the axes perpendicular to the main (long) axis is hindered. This is topochemically unfavorable. This is the reason why in the nematic state the rate of polymerization is lower than that in the isotropic liquid state at the same temperature.

3.1.4. Effect of Mesophase on the Stereospecificity of the Polymerization

Blumstein et al.¹⁴⁵ investigated the effect of the mesophase in which the polymerization takes place on the stereoregularity of the resulting polymer. *p*-Methacryloyloxy benzoic acid was polymerized in the nematic phase of 4-heptyloxybenzoic acid and in the smectic phase of 4-cetyloxybenzoic acid. The excess of isotactic components observed at low conversions, diminished at higher conversions and approached that observed in *reference polymers prepared in solution*. At the same time, the percentage of atactic components increased, indicating that the randomness of the polymerization increased. This was suggested to be due to the fact that the polymer chains destroyed the anisotropic organization of the bulk liquid crystalline media. These effects were observed in the nematic as well as in the smectic phase. The results were confirmed in a study performed by Saeki et al.¹⁴⁶ Polymerization of cholesteryl methacrylate in the mesophase and in the isotropic phase gave no significant difference in tacticity.

3.1.5. Cationic Bulk Polymerization of Mesogenic Vinyl Ethers in the Liquid Crystalline Phase

The liquid crystalline vinyl ethers 49-52 were polymerized cationically in both anisotropic and isotropic monomeric melts, using either thermal or photochemical initiation by the onium salts 53 and 54.^{147,148}

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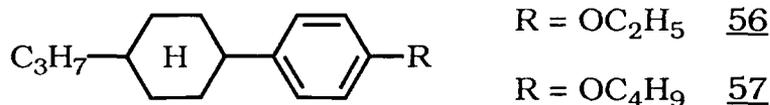
In the case of photochemical initiation, a redox system based on an onium salt, e.g. 54, and a free radical photoinitiator or a photosensitizer, e.g. 55, were used in order to increase the spectral response. High molecular weight polymers were produced even at temperatures above 100 °C (Table VI). Further, the molecular weight distribution was at the same time kept very narrow for a cationic polymerization performed at such a high temperature and the conversions were also very high.

Usually, extensive chain transfer occurs when vinyl ethers are polymerized at room temperature and only low molecular weight polymers are obtained. Apparently, the propagation cation in this type of system is stabilized, and thus, the extent of chain transfer reactions is reduced. One possible reason is that the predominant chain transfer reaction is to counter-anion and not to monomer, and the low basicity of the PF_6^- and SbF_6^- anions may be responsible for the small extent of chain transfer reactions. Another possible explanation, at least at the low temperatures, is that the growing center is stabilized by the nucleophilic tetramethylene sulfide ring released from the onium salt initiators, by analogy to sulfide stabilization of the cation in

living cationic polymerization of vinyl ethers. No differences in polymerization rate or polymer molecular weight were observed between polymerizations initiated in the nematic or the isotropic state of the monomer. Highly ordered 30-50 μm films were produced by the polymerization of films of monomers oriented in the nematic state. The films of the resulted polymers despite being in a smectic A liquid crystalline state, were completely transparent also at room temperature. Apparently, the number of light scattering crystal boundaries were very few, which indicates the very high degree of order in the material. The resulted polymer film can be considered as being almost a mono-domain or a single crystal liquid crystal. Presently, this polymerization technique seems to represent the most reliable method to produce highly oriented films of side chain liquid crystalline polymers.

3.2. Polymerization of Acetylene on the Surface of a Liquid Crystalline Phase

Araya et al.¹⁴⁹ studied the polymerization of acetylene initiated with Ziegler-Natta catalysts on the surface of flow oriented nematic liquid crystals 56 and 57 and of an equimolar mixture of 56 and 57.



equimolar mixture of 56 & 57 : k 20 n 34 i i 34 n 0 k

Polymerizations were performed at 18 °C. The Ziegler-Natta catalyst Ti(OC₄H₉)₄/Al(C₂H₅)₃ was dissolved in the liquid crystal. The mixture was introduced in a Schlenk flask and coated onto the walls by swirling. After the flask was brought back into its upright position, acetylene was introduced into the Schlenk flask. Polymerization took place on the downflowing liquid crystalline mixture. Scanning electron microscopy showed that a highly oriented fibrillar polyacetylene film was the result of the polymerization. The authors concluded that the fibrillar crystals grew together in the same direction due to an alignment effect of the liquid crystalline molecules.

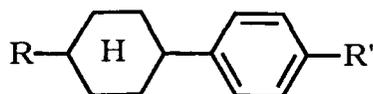
In an extended investigation the same group¹⁵⁰ provided further evidence that the oriented fibrillar structure of the formed polyacetylene film is the result of the orientation caused by the mesophase. Polymerizations performed on a non oriented nematic surface (partially ordered polyacetylene film resulted) or on a flowing liquid crystalline mixture in the isotropic state, both produced polymers showing an aggregation of randomly oriented fibrils. However, the authors claimed, that in the case of the non-oriented nematic surface, local orientation of the fibrils could be found, corresponding to a nematic domain of the liquid crystal. The

polymerization time was 1 minute and 1 μm thick films were produced. By doping the oriented polyacetylene films with I_2 or AsF_5 they managed to produce polymer films with one of the highest electrical conductivities reported so far.¹⁵¹ The polymerization temperature was 10-13 $^\circ\text{C}$.

In another publication¹⁵², the same authors determined the order parameter of the polyacetylene film to be 0.57, a value that approximately equals the value of the nematic liquid crystal. They also concluded that it is only in the beginning of the polymerization that the orientation of the fibrils is effected by the alignment effect of the liquid crystal molecules (as the film gets thicker, the orientation gets worse). The size of the resulted polymer fibrils was 100 nm in diameter and 10 μm in length when the polymerization temperature was 18 $^\circ\text{C}$.

Akagi et al. have also polymerized acetylene on ordered media under the influence of a magnetic field.¹⁵³ The liquid crystalline compound and Ziegler-Natta catalyst were the same as those described previously. The polymerizations were carried out in a flat-bottomed container placed in a Schlenk tube that was placed in the magnet (2-14 kGauss). The polymerization temperature was 10-15 $^\circ\text{C}$. A high degree of fibril alignment was obtained and the diameter of the fibrils was of about 800-1000 Å . Even higher values of electrical conductivity than those for gravity flow aligned films were achieved, when the films were doped with I_2 (i.e. 10^4 S/cm). A summary of this group's work on polymerization of acetylene in ordered media is given in reference 154.

Finally, this group has also performed this type of polymerizations at low temperatures (-10 to -60 $^\circ\text{C}$).¹⁵⁵ This was possible by the use of 3-6 component systems of nematic liquid crystals of phenylcyclohexane derivatives of the general structure 58.



R = alkyl

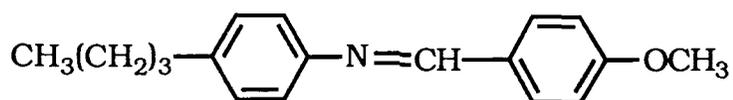
R' = alkyl or alkoxy

58

Films with a high (85-94 %) cis content were produced. They had the same properties as those previously described.

Montaner et al.¹⁵⁶ have also used the Araya and Akagi polymerization method to produce highly oriented polyacetylene films. They used the same Ziegler-Natta catalyst and the same nematic liquid crystalline compounds. They combined the gravitational flow and the magnetic methods for the alignment of the liquid crystals. The strength of the field was 47 kG. The resulted polymers had a trans/cis ratio of 2/3. The electrical conductivity of the resulted polymer was $\sim 2 \times 10^4 \Omega/\text{cm}$. In another paper¹⁵⁷, the same authors reported that the polyacetylene containing cis and trans structural units presented a three-dimensional local order.

Aldissi¹⁵⁸ has reported the polymerization of acetylene at 25 °C in the nematic phase of 59.

59

nematic range 19-30 °C

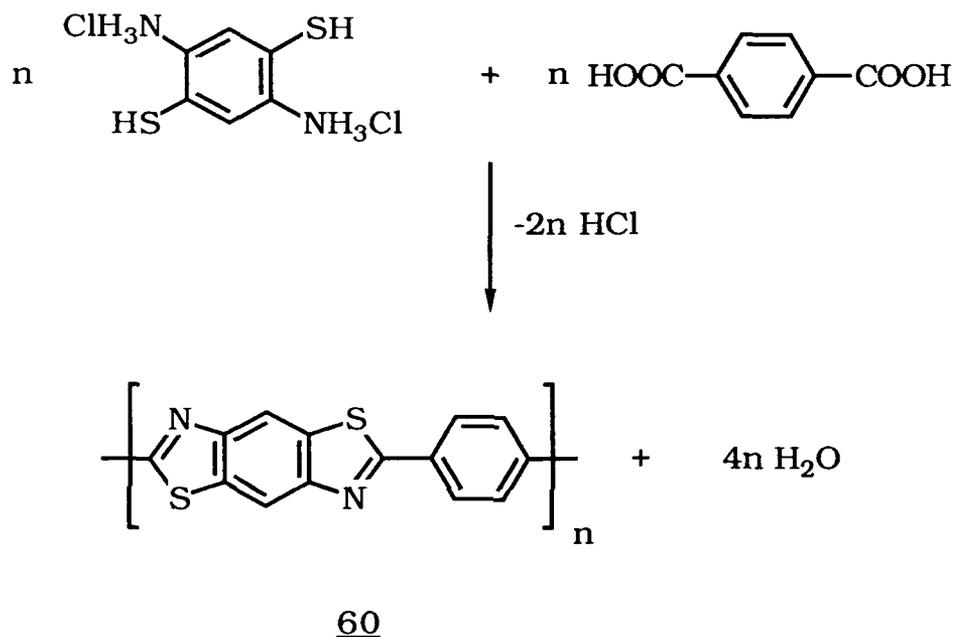
The liquid crystals were oriented in a magnetic field of ~ 4 kG. He used the same Ziegler-Natta catalyst as the earlier investigators. This was the first reported polymerization of acetylene in a magnetic field. However, the orientation achieved was much lower than the one reported by Akagi et al.¹⁵³ and Montaner et al.¹⁵⁶ probably due to the weaker magnetic field. In later publications,^{159,160} Aldissi reported some improvements of his polymerization technique. The magnetic field

was stronger (9kG), a flow was used in addition to the magnetic field orientation and a 1:1 4-(trans-4-n-propylcyclohexyl)-ethoxybenzene/4-(trans-4-n-propylcyclohexyl)-n-butoxybenzene liquid crystal mixture that had been used successfully earlier. The polymerization temperature was 0-5 °C. The AsF₅ doped films showed conductivities of $\sim 1.5 \times 10^4 \Omega/\text{cm}$. Both the molecular (chains) and the supramolecular (fibrils) levels of polyacetylene were oriented.

3.3 Polymerization in Lyotropic Liquid Crystalline Media

3.3.1. Synthesis of Poly(p-phenylenebenzobisthiazole)

The synthesis of poly(p-phenylenebenzobisthiazole) (60) 2,5-diamino-1,4-benzenedithiol dihydrochloride and terephthalic acid¹⁶¹ in polyphosphoric acid was investigated as a function of monomers and polymer concentrations.

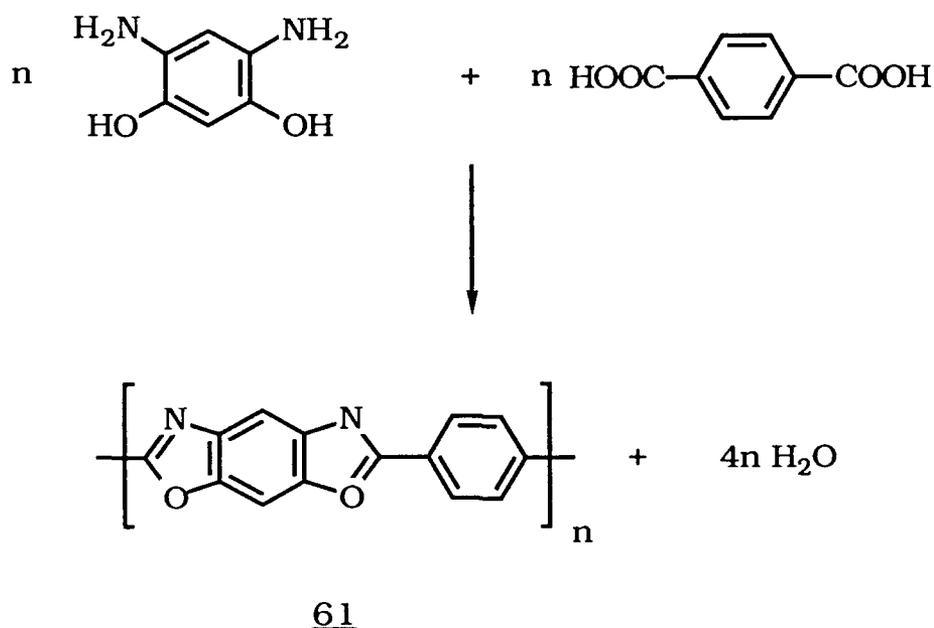


When the concentration of the polymer in the reaction mixture reached the isotropic-nematic phase transition (5 wt %), for a polymerization in which the final polymer concentration is 15 wt %, a dramatic increase of about 5 times in reaction rate was observed (Figure 3). This abrupt increase in the reaction rate was interpreted as a quantitative description of the mesophase-enhanced polymerization by which the enhancement in kinetics is due to the alignment of rigid-rods in the ordered phase. In contrast, when the same synthesis is conducted at low concentrations (less than 2-3 wt % final polymer in solution) the rate of polycondensation decreases with the increase in molecular weight throughout the entire reaction as expected for a classic step polymerization reaction. On further polymerization the reaction rate decayed

exponentially and this was assigned to be a function of the amount and reactivity of aromatic acid used as end-capping agent, the reactivities of side-reactions and the molecular weight of the polymer.

3.3.2. Synthesis of Poly(p-phenylenebenzobisoxazole)

Cotts and Berry¹⁶² have investigated a very similar system; i.e. the synthesis of poly(p-phenylenebenzobisoxazole) (61) from 4,6-diamino-1,3-benzenediol dihydrochloride and terephthalic acid in polyphosphoric acid.



They found that the polymerization rate decreased monotonically with increasing molecular weight of the polymer. Based on this, they stated that the polymerization rate for the condensation of rods was diffusion controlled. However, their concentration of polymer was always kept at 0.5-2.0 wt % , i.e. below the transition from the isotropic to the liquid crystalline phase.

3.3.3. Synthesis of Poly(p-phenylene terephthalamide)

Poly(p-phenylene terephthalamide) was synthesized in dimethylacetamide.¹⁶³ First an oligomer gel was made by reaction of the

monomers in a vigorously stirred solution. The hard gel, consisting of oligomers and solvent, was then allowed to stand still for several hours. The subsequent polymerization resulted in an increase of the molecular weight of the oligomers from ~15,000 to ~57,000 and the molecular weight distribution was narrow. The resulting polymer was a mass of fibers having a secondary structure similar to cotton or linen. The authors explained the fiber formation to be due to the parallel arrangement of oligomeric chains to the mechanical shearing direction in combination with end-to-end alignment by electrostatic interactions and the formation of dimethylacetamide solvent bridges. The completion of the molecular growth leads to the collapse of the solvent bridges with subsequent expulsion of solvent molecules leaving fibrils and microcleavages between them.

3.3.4. Emulsion Polymerizations in Lyotropic Mesophases

Acrylamide was polymerized in a lamellar liquid crystalline phase consisting of oil/water/surfactant/sodium acetate/acrylamide/AIBN.¹⁶⁴ The polymerization induced a structural change from the initial swollen lamellar phase to the final homogeneous dispersion of spherical particles. The polymerization immediately induced phase-separation and monomer transfer from the organized mesophase to the disordered isotropic phase. This result was accounted for by the monomer acting as a co-surfactant at the interface and the flexible and fluctuating nature of the labile interfaces of multicomponent systems.

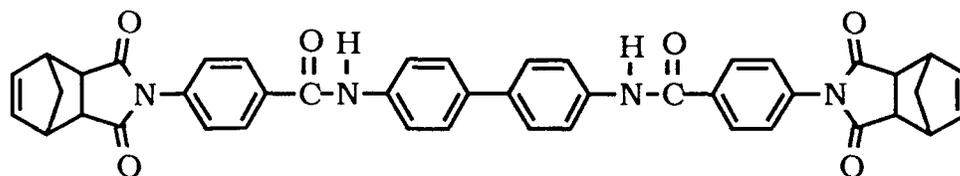
Polymerization of sodium undecenoate in a lyotropic solution of water and sodium undecenoate initiated by ammonium persulfate, resulted in a phase change from a two-dimensional hexagonal close packing of cylinders to a lamellar liquid crystalline phase.^{165,166} The polymerization was performed between glass-slides at 60 °C. After 24 h, the hexagonal phase disappeared and the lamellar phase appeared on subsequent cooling to 20 °C. The degree of polymerization of the resulted polymer was about 250-300.

The polymerization of one or more components of a lyotropic liquid crystal in the bicontinuous cubic phase (simultaneous continuity of hydrophilic and hydrophobic components together with cubic crystallographic symmetry) has been performed¹⁶⁷. The first system consists of didodecyl dimethylammonium bromide (DDAB)/water/methyl methacrylate in a % ratio of 55.0/35.0/10.0 with 0.004 g/mL of azobisisobutyronitrile as initiator. After 1 week of equilibration at 23 °C, the samples were polymerized photochemically using four 340 nm UV lamps and irradiation for 36 hours. After removal of the soluble components a microporous material with a highly-branched, monodisperse, triply periodic pore space structure was obtained. The second example investigated by the same authors involved a non-ionic system of dodecyl hexaethylene glycol ether/water/acrylamide. The acrylamide concentration was 19.96 wt % of the aqueous phase with 1.1 wt % (of the acrylamide) hydrogen peroxide as the initiator. The aqueous phase formed 30.30 wt % of the total mixture. The polymerization was performed under a nitrogen atmosphere at 23 °C and was initiated via UV irradiation. Also in this case a microporous material resulted (a polymerized cubic structure).

3.4. Crosslinking in Liquid Crystalline Phase

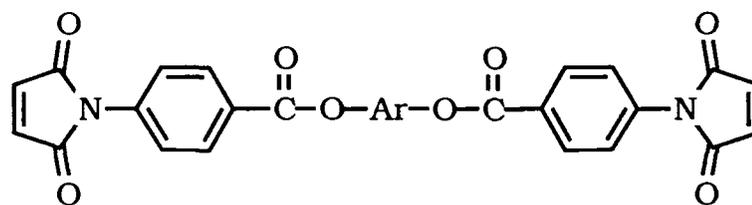
3.4.1. Synthesis of Liquid Crystalline Thermosets

End functionalized rigid-rod monomers have been polymerized in the nematic state.¹⁶⁸ 62 polymerized thermally at 350 °C within about 10 seconds after melting and the nematic texture of the monomer was preserved in the crosslinked polymer.



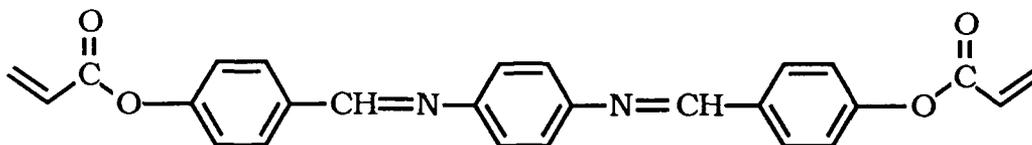
62

63 - 65 crosslinked immediately after melting into a nematic phase and the nematic texture was also preserved in the resulted crosslinked polymers.

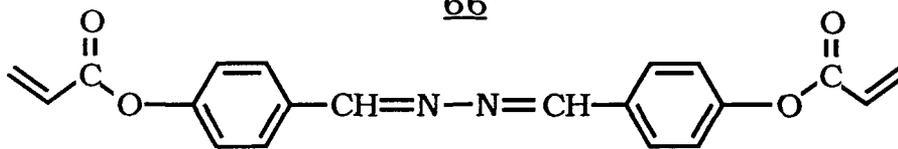


	<u>Ar</u>	<u>T_m (°C)</u>
<u>63</u>		278
<u>64</u>		299
<u>65</u>		287

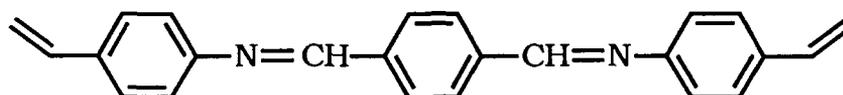
A number of difunctional Schiff base monomers (66-68) have been polymerized in their mesomorphic state.¹⁶⁹



66



67

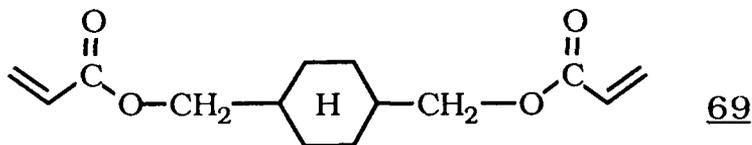


68

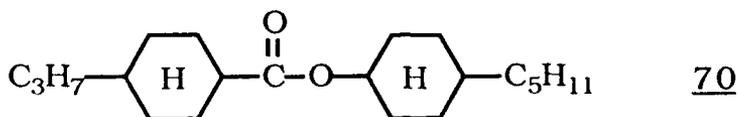
The phase of the monomer was sometimes "frozen-in" but in other cases a phase of higher order resulted after polymerization i.e., the nematic monomer changed into a smectic polymer. According to the authors, this phenomenon seems to be dependent on the ability of interacting side groups to pack into a layered arrangement without disturbing the regular disposition of the polymer backbone. In some cases, the monomer was oriented in a 4.5 kG magnetic field. A well oriented polymer resulted.

3.4.2. Polymerization of Bisacrylic Monomers in a SB Solvent

The bifunctional acrylate monomer 69 was polymerized in the SB phase of 70.¹⁷⁰



69

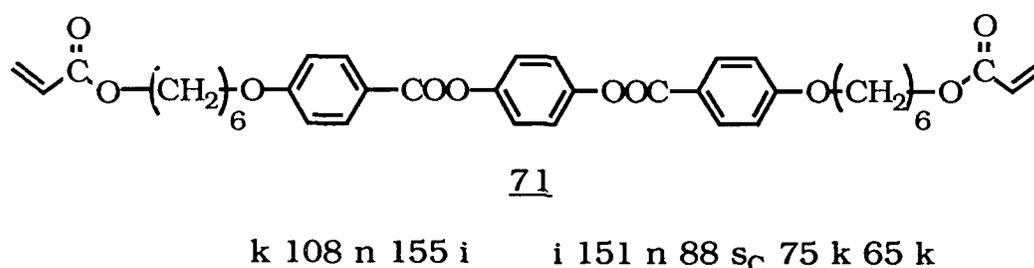


70

By using differential scanning calorimetry, it was shown that at a certain conversion, the polymer started to aggregate from the liquid crystalline solvent. After this, the polymer chains possibly grew upon or between the faces of the SB layers. The polymerizations were carried out utilizing an excimer laser (multilaser-306 nm).

3.4.3. Oriented Polymer Networks

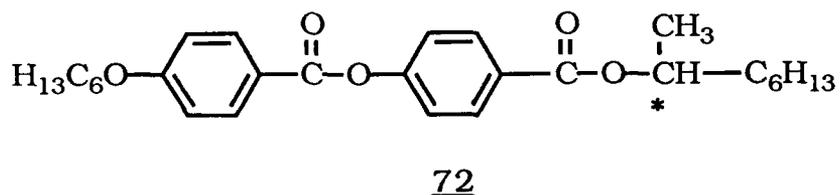
Oriented polymer networks were synthesized through the orientation and subsequent photopolymerization of 71.¹⁷¹



During polymerization the order of the mesogens was "frozen-in". In the highest oriented state of 71 a small reduction of the degree of order was observed, whereas at higher temperatures and lower ordering of 71 the uniaxial orientation increased upon reaction. The orientation of the networks was maintained upon heating of the cured films. Above 90 °C the polymerization reaction proceeded faster for the liquid crystalline diacrylate compared to an isotropic diacrylate. The authors suggested an explanation for this result based on thermodynamic considerations. The ceiling temperature of an acrylate increases with increasing the initial state of order. Above the transition to isotropic, the equilibrium conditions of the non-mesogenic acrylates are valid again (steep decrease of the polymerization rate at increasing temperatures). Another explanation was based on the fact that the Trommsdorff effect should lose its importance at higher temperatures. The effect of substituents on the central aromatic group¹⁷² and of the length of the spacer,¹⁷³

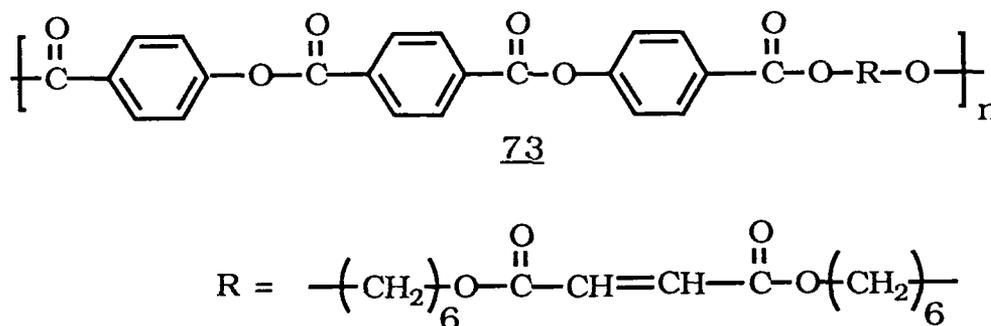
on the properties of the mesogenic monomers and the formation and properties of the oriented networks, have also been investigated. As was the case for the polymerization of ordered monoacrylates (see Chapter 3.1.2), the order was maintained during the polymerization resulting in densely crosslinked oriented networks.

By the addition of the chiral compound 72 to the diacrylate 71, networks with a helicoidal ordering of the mesogenic crosslinks were produced.¹⁷⁴



3.4.4. Crosslinkable Liquid Crystalline Main-Chain Polymers

Liquid crystalline main-chain polyesters containing fumarate ester moieties in the spacer (73) have been synthesized and crosslinked by copolymerization with styrene.¹⁷⁵



Films containing the polymer 73 and styrene were cast from chloroform solution and crosslinked at temperatures between 130 and 180 °C. The thermal transitions of polymers 73 are summarized in Table VII. The crosslinked polymers were infusible and exhibited strong birefringence above the softening point. Cooling

from the isotropic state led via a liquid crystalline phase to an oriented solidified polymer.

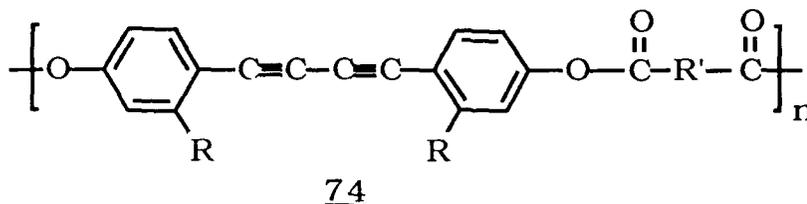
3.4.5. Cholesteric Polymer Networks from Nonmesogenic Monomers

Tsutsui and Tanaka¹⁷⁶⁻¹⁷⁸ reported in a series of publications some studies on the preparation of poly(butyl acrylate) networks synthesized in a lyotropic solvent. Butyl acrylate, containing 0.5-10 wt % ethylene glycol dimethacrylate was polymerized in the cholesteric phase of poly(γ -butyl-L-glutamate) using benzoyl peroxide as initiator at 60 °C. The network swelled in organic solvents and the swollen material exhibited a cholesteric mesophase. When the polypeptide component was removed the mesomorphic behavior of the extracted network was lost. However, by swelling in organic solvents the mesomorphicity of the network was restored. A high density of crosslinking was essential to achieve a cholesteric organization in the swollen vinyl polymer without polypeptide as a mesogen. The anisotropic structure of the network was explained by the transfer of topologically specific cholesteric geometry from the original liquid crystalline phase to the network.

The same authors¹⁷⁹ also used a photoinitiated polymerization to produce crosslinked cholesteric polymers. Triethylene glycol dimethacrylate was mixed with poly(γ -butyl-L-glutamate) at ratios of 60/40, 55/45, 50/50, 45/55 respectively, and 2 % benzophenone. Polymerizations were performed utilizing a high-pressure mercury lamp with the sample placed between glass slides (with a 0.2 mm gap) at e.g. 20 and 30 °C. It was possible to produce polymer films that selectively reflected visible light at any desired wavelength just by controlling the triethylene glycol dimethacrylate/poly(γ -butyl-L-glutamate) ratio and the polymerization temperature.

3.4.6. Liquid Crystalline Polymers Containing Diacetylenic Groups

Diacetylenic polymers and copolymers of the general structure 74 have been prepared.¹⁸⁰



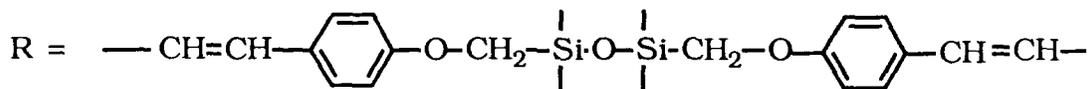
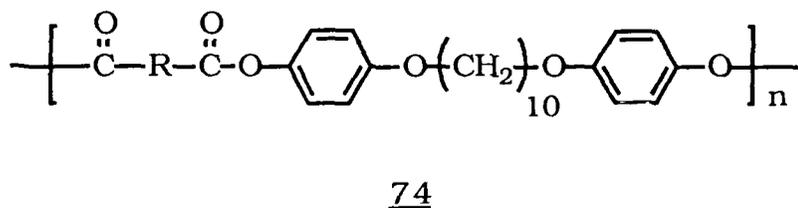
R = H, CH₃

R' = different methylene sequences
branched and unbranched

All polymers showed liquid crystalline phases. At the temperatures of their mesophases (above 175 °C) all these polymers reacted via the triple bonds giving crosslinked structures that impeded the liquid crystalline phase stability.

3.4.7. Photochemical Crosslinking of Main-Chain Liquid Crystalline Polymers Containing Cinnamate Groups in the Spacer

Main-chain liquid crystalline polymers containing siloxane and cinnamate ester groups (75) were synthesized.¹⁸¹



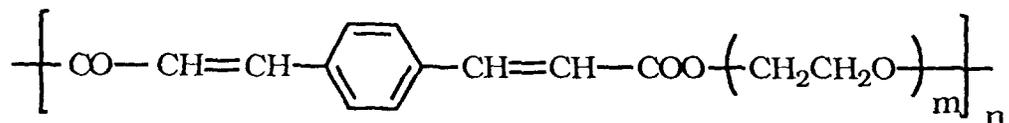
The polymers were crosslinked by photolysis which leads to cyclobutane ring formation (Scheme 4). The reaction was performed in the amorphous, frozen

nematic, nematic, and isotropic states as well as in solution. Photolysis of a few mm thick film at 313 μm for 1 hr in the amorphous state at 30 $^{\circ}\text{C}$ gave a yellow solvent resistant film which contained about 50 % cinnamate groups being crosslinked. This crosslinking reaction is accompanied by a photo-Fries side-reaction giving o-phenol derivatives which produce a colored polymer. When the crosslinking reaction is carried out in the isotropic state at 130 $^{\circ}\text{C}$ the photo-Fries product formation is enhanced while at 30 $^{\circ}\text{C}$ (i.e. in the amorphous phase) it is quite low. The reaction in mesomorphic phase at 88 $^{\circ}\text{C}$ represents an intermediate case. The same research group¹⁸² used a very similar polymer containing nine methylenic units in the spacer instead of ten for photo-optical recording on free-standing films. Amorphous films were irradiated with a laser (325 nm). The irradiation resulted in crosslinking (insolubility), photo-Fries product formation (yellow color) and a transition from the glassy to the nematic state (birefringence) due to temperature elevation by heat transfer.

The photo-Fries reaction reported to occur together with cyclization in the previous paper was eliminated when the aryl ester group of the cinnamate was replaced with cycloaliphatic groups.¹⁸³ In contrast to the aryl ester polymer, a birefringent film was formed upon film casting. This was assigned to the formation of a lyotropic nematic mesophase when the solvent was evaporated.

3.4.8. Topochemical Photodimerizations in Liquid Crystalline Polymers

Ikeda et al.¹⁸⁴ studied topochemical photodimerization of a liquid crystalline polyester based on p-phenylene diacrylic acid and various ethylene glycol derivatives (76,77).



$$\underline{76} : \quad m = 2 \quad M_n = 7,000$$

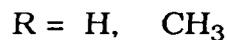
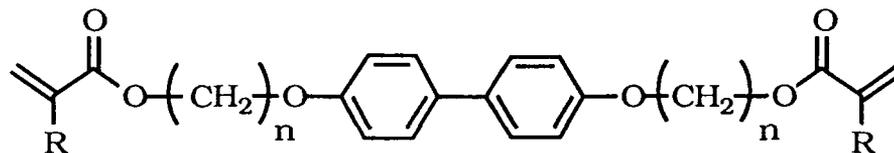
$$\underline{77} : \quad m = 3 \quad M_n = 7,200$$

As expected, irradiation of the polymer with monochromatic light of 313 nm, led to photodimerization with subsequent cyclobutane ring formation and crosslinking. The efficiency of the photodimerization leading to interchain crosslinking was significantly higher in the nematic state than in the glassy or isotropic state. This was interpreted in terms of low mobility in the glassy state and a favored orientation of the photoreactive moieties in the liquid crystalline state compared to the isotropic state. The T_g of the irradiated samples was shifted to higher temperatures and the nematic to isotropic transition disappeared.

Excimers were found to be formed much more effectively in the liquid crystalline state than in the isotropic state, due to the parallel orientation of the chromophores¹⁸⁵. In addition, their lifetime was longer in the more oriented system because of the restricted mobility.

3.4.9. Photo-crosslinking of Bifunctional Liquid Crystalline Monomers

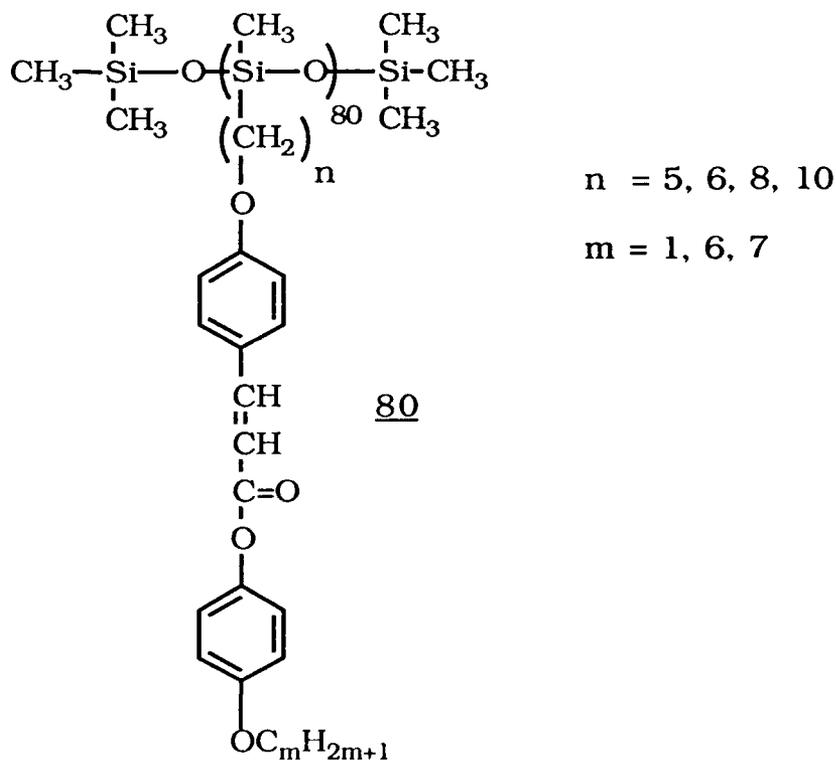
Bifunctional liquid crystalline acrylates (78) and methacrylates (79) have been photopolymerized in their smectic state.¹⁸⁶ The polymerizations were performed on samples cooled down from the isotropic state to room temperature between glass plates giving films of 0.2-0.4 mm thickness.



78 79

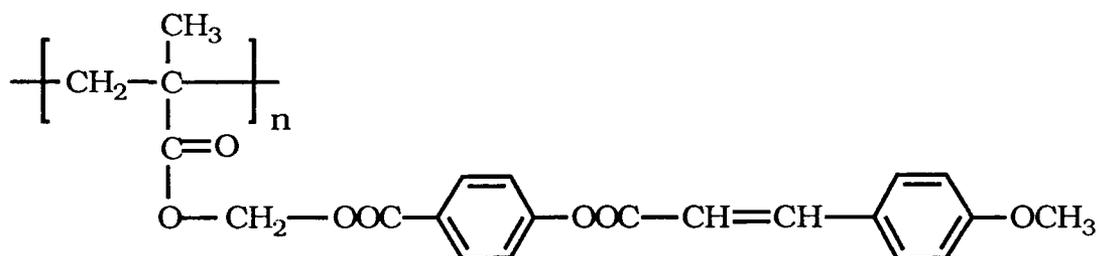
3.4.10 Photo-crosslinkable Side-Chain Liquid Crystalline Polysiloxanes

A two-step synthetic procedure was reported for the synthesis of side-chain liquid crystalline polysiloxane (80) elastomers, which can be crosslinked by ultraviolet irradiation of their linear side groups containing cinnamoyl moieties in the glassy state.¹⁸⁷ These systems allow the linear polymer to be aligned and then by irradiation with UV light the order is "frozen-in" in the macroscopically oriented side-chain liquid crystalline polysiloxane elastomers. The crosslinking reaction takes place through the phenyl cinnamate groups that also function as mesogens.



All the polymers showed only a sC mesophase and, depending on the length of the spacer, the polymers were also crystallizable or noncrystallizable. No orientation results were however reported so far.

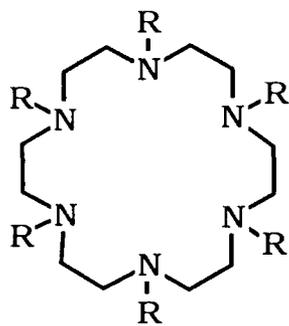
The photochemistry of films of the polymer 81 was investigated and compared with that of non-liquid crystalline side-chain polymers containing methoxycinnamate groups.¹⁸⁸ The relative quantum yield of cyclobutane formation was about a factor 8 times higher for the liquid crystalline methoxycinnamate polymer, and this value was close to the theoretical value.



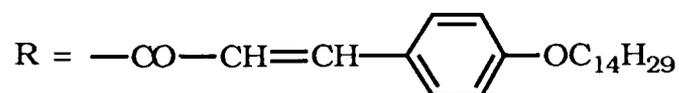
81 g 21 n 168 i

3.4.11. Photochemical Behavior of a Discotic Cinnamoyl-Substituted Azacrown Derivative

Compound 82 was irradiated with UV light in solution as well as in bulk state.¹⁸⁹ A 200 W high pressure Hg lamp and either an interference filter of 296 nm, 313 nm or a cut off filter (WG 305) with light intensities of 2 mW/cm² and 470 mW/cm² were used.



82



k 217 °C D_{hd} 233 °C i

In cyclohexane, i.e. a poor solvent, oligomers consisting of 2-20 molecules bound together in a tube-like array were formed through intracolumnar photocycloaddition between adjacent molecules in the columnar aggregates. However, in a good solvent like chloroform, no column aggregates were formed and photolysis resulted in cleaved photoproducts and intramolecular dimerization. In the bulk phase, E/Z-photoisomerization took place which destroyed the mesophase and an isotropic phase was formed. Continued irradiation resulted in crosslinking.

3.5 Anisotropic Gels

Mixtures of liquid crystalline diacrylates (83) and low molar mass liquid crystals (84) without reactive groups were photopolymerized in the nematic state^{190,191} to produce liquid crystalline gels (Figure 4). The behavior of the low molar mass liquid crystals was found to be dominated by the presence of the network, i.e. even at temperatures far above their isotropization, they remained partially oriented. Two populations of low molar mass liquid crystals were found: a) molecules strongly bound to the network which showed no nematic-isotropic transition and b) free low molar mass liquid crystalline molecules. At a network concentration of 30 % w/w, 80 % of the low molar mass liquid crystalline molecules were bound and did not undergo the nematic-isotropic transition. If the network concentration was 50 % or higher no detectable melting or nematic-isotropic transition were found.

3.6 Liquid Crystalline Crosslinked Elastomers

Finkelmann et al.,¹⁹²⁻¹⁹⁵ have synthesized liquid crystalline crosslinked elastomers (85a-g) based on liquid crystalline polysiloxanes (Scheme 5). The glass transition and usually the liquid crystalline to isotropic transition of the crosslinked elastomer is shifted to lower temperatures due to the softening effect of the crosslinking agent (Table VIII). A very low percentage of crosslinking caused no change in the behavior of the liquid crystalline phase.

By incorporation of chiral comonomers it was possible to synthesize chiral elastomers. The opacity present in the elastomers in the liquid crystalline state, disappeared upon stretching the sample since the mesogenic groups became oriented. Thermoelastic measurements¹⁹³ showed that the refractive force in the liquid crystalline state depended only on length and temperature and based on this, it was concluded that the liquid crystalline phase was homogeneous and had reached its internal equilibrium.

The mechanical behavior of these crosslinked elastomers was summarized as follows: "In the isotropic and glassy states, their properties are similar to those of conventional elastomers. At the isotropic to liquid crystalline phase transformation and in the liquid crystalline state, the elastomeric behavior strongly differs from the behavior of conventional elastomers. At T_c (clouding) the linear thermal expansion coefficients as well as the stress behavior indicate reorientation processes of the mesogenic side-chains, which convert the isotropic elastomers into macroscopically anisotropic samples. Consequently, the anisotropic physical properties in the homogeneous liquid crystalline state are determined not only by the network of the polymer backbone but also by the orientation of the mesogenic side-chains with respect to the direction of the mechanical force". X-ray measurements showed that the mesogenic groups were uniformly oriented in the nematic phase. Depending on if the spacer consisted of 3 or 4 methylene units, an optically biaxial or uniaxial

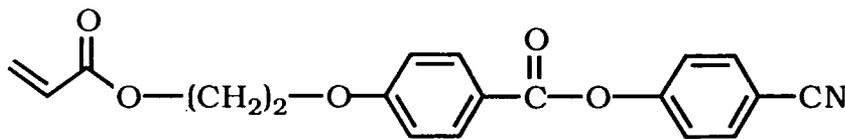
liquid crystalline network was formed upon deformation.¹⁹⁴ Only the orientations of the directors with respect to the axis of deformation were changed, not the structure of the nematic phase. Still, after extensive IR-dichroism measurements, the orientation behavior of these liquid crystalline elastomers is not yet understood.¹⁹⁵ Crosslinked liquid crystalline polymers 86 were swollen with and dispersed in nematic low molar mass liquid crystals (phenyl-cyclohexane mixture 1132 TNC from Merck)¹⁹⁶ (Scheme 6). The shape of the polymer changed if an electrical field was applied and the shape variation depended on the degree of swelling.

Two types of orientation of the mesogenic groups were found for stretched crosslinked liquid crystalline side-chain polymers 87¹⁹⁷ (Scheme 7). For polymers with $R_1 = \text{CH}_3$, $n = 6$, $R_2 = \text{OCH}_3$, $x/y = 1/0.05$ and for polymers with $R_1 = \text{CH}_3$, $n = 6$, $R_2 = \text{OC}_4\text{H}_9$, $x/y = 1/0.05$, the mesogenic groups oriented perpendicular to the direction of strain. For polymers with $R_1 = \text{H}$, $n = 6$, $R_2 = \text{OCH}_3$, $x/y = 1/0.05$, $R_1 = \text{H}$, $n = 2$, $R_2 = \text{OCH}_3$, $x/y = 1/0.05$ and $R_1 = \text{H}$, $n = 6$, $R_2 = \text{CN}$, $x/y = 1/0.08$, and for polymers 88 (Scheme 8) the mesogenic groups oriented parallel to the direction of strain. This was considered as a proof of the ability of the spacer to decouple the mesogenic groups from the polymer chain.

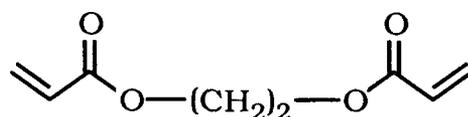
Two types of chiral (n^* , sC^*) combined liquid crystalline elastomers have been synthesized.^{198a,b} They consist of polymers containing mesogenic groups both in their main-chain and as side groups. The first series of polymers (89a-91a) (Scheme 9 and Table IX) were crosslinked in the isotropic solution due to the immiscibility of the liquid crystalline polymer and the siloxane. X-ray measurements showed that the helical superstructure of the cholesteric and chiral smectic C phases could be untwisted by stretching the elastomers 89b-91b to a strain level of 300 %. A different synthetic route for the second series of elastomers (92-95) (Schemes 10, 11 and Table X) allowed their crosslinking to be

carried out in the mesophase of the linear polymer by either photochemical or thermal initiation.

By copolymerization of 96 and 97, using AIBN at 60 °C in chlorobenzene solutions under vacuum, liquid crystalline polyacrylate crosslinked elastomers were synthesized.^{198c}



96



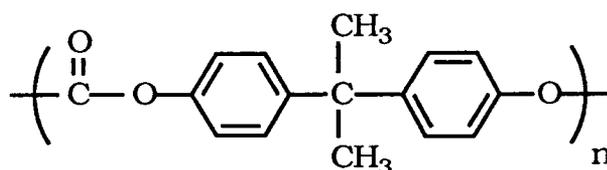
97

Crosslinking, up to 10% of structural units produced elastomers with properties similar to those observed in the corresponding linear polymers. However, highly crosslinked samples lost the nematic-isotropic phase transition although some birefringence was observed. The nematic-isotropic transition temperature decreased while the glass transition temperature increased with increasing the degree of crosslinking. Recently, it has been theoretically predicted^{199a} and experimentally demonstrated that chiral crosslinked elastomers (both cholesteric^{199b} and chiral smectic C^{199c}) represent a new class of piezoelectric materials.^{199d}

3.7 Liquid Crystalline Membranes

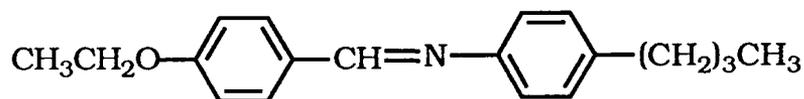
3.7.1. Gas Permeability through Immiscible Blends of Amorphous Polymers and Low Molar Mass Liquid Crystals

In films of composite membranes consisting of immiscible blends of amorphous polymers (98) with low molar mass liquid crystals (99) and containing up to 60 wt % liquid crystal, the permeability coefficients to hydrocarbon gases increased 100-200 times in the vicinity of the crystal to liquid crystal transition temperature.^{200-202,204}



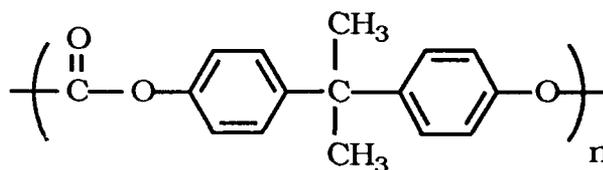
Polycarbonate (98)

+



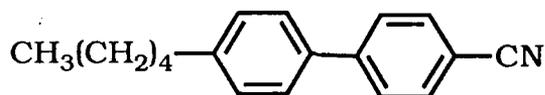
N-(4-ethoxybenzylidene-4'-*n*-butylaniline) (99)

At 60 wt % liquid crystal, the composite membrane can be handled as a homogeneous medium when considering gas permeation. The same authors²⁰³ also investigated the effect of an electric field on the permeability of *n*-C₄H₁₀ and He gases in the system of 98 and 100.



Polycarbonate (98)

+



60 wt % 4-cyano-4'-n-pentyl biphenyl (100)

The permeability coefficient (P) to $n\text{-C}_4\text{H}_{10}$ and He gases increased approximately 80 and 5 times respectively at the crystalline to liquid crystalline transition region. The magnitude of permeability (P) to helium is greater than that to $n\text{-C}_4\text{H}_{10}$ below the phase transition temperature, but above, it is smaller. This result is most likely due to the different permeation mechanism below and above the transition, i.e., the diffusion controlled below the transition and the solubility controlled above the transition. The orientation of the liquid crystalline molecules in the electric field caused an increase of the gas permeability, the magnitude of the increase depending on the magnitude of the applied voltage. Also, the dramatic increase of P at the crystalline-nematic transition may arise from an induced activation of thermal molecular motion or increased vacancy fractions. The permeability of water through a polymer/liquid crystal composite membrane is similar to that observed for gases.²⁰⁵

Composite membranes composed of 98/99, 98/102, 101/99 and 101/103 (Figure 5) at a weight ratio of 40/60 were prepared.²⁰⁶ The magnitude of P_{O_2} increased by about 10-20 times within a few degrees in the vicinity of the crystal to

liquid crystal transition temperature. The separation ability of oxygen versus nitrogen reached a maximum value around the same phase transition region.

The permeability coefficients to oxygen (PO_2) and nitrogen (PN_2) gases through a 40/60 polyvinyl chloride/N-(4-ethoxy-benzylidene)-4'-n-butylaniline membrane showed a several-tenfold increase at the crystalline to nematic transition temperature of the liquid crystal.²⁰⁷ An unusual behavior of the relationship between PO_2 and the separation factor PO_2/PN_2 was observed above the crystalline to nematic transition, i.e. the factor PO_2/PN_2 increased with increasing PO_2 . The reasons for this behavior could not be clarified.

Washizu et al.²⁰⁸ investigated the oxygen permselectivity in a composite membrane composed of polyvinyl chloride/N-(4-ethoxy-benzylidene)-4'-n-butylaniline/perfluorotributylamine/Pluronic L44 (polyoxyethylene/polyoxypropylene ABA block copolymer surfactant) at a weight ratio of 40/60/7.2/7.2 respectively. The composite membrane exhibited excellent oxygen permeability and permselectivity as compared to a composite membrane without perfluorotributylamine. The composite membrane showed a unique trend namely PO_2/PN_2 increased with increasing PO_2 in contrast to that for common gas separation membranes.

3.7.2. Photoresponsive Permeation in Composite Membranes of Polymer/Artificial Lipid/Azobenzene Derivative

The permeation of water and K^+ in a ternary composite membrane of polyvinylchloride (PVC)/dioctadecyl dimethylammonium bromide (DOAB)/p- ω -hydroxy-propyloxy-p'-dodecyloxy azobenzene (AZO) in a weight % ratio of 85/13.1/1.9 was investigated.²⁰⁹ Irradiation of the membrane with UV light at temperatures where the DOAB was in its liquid crystalline state, initiated the trans→cis isomerization of the azo compound. This isomerization caused the formation of "channels" in the DOAB bilayer of the membrane with a subsequent

increase in permeation. Below the transition from crystalline to liquid crystalline phase no increase was observed even though the isomerization took place.

Similar synthetic bimolecular membranes without azo molecules have also been investigated for their permeability properties.²¹⁰ The permeability of water through a polyvinylchloride (PVC)/dioctadecyl dimethylammonium bromide and PVC/sodium dihexadecyl phosphate membranes showed a distinct increase at the crystalline to mesomorphic phase transition of the liquid crystalline compound. This increase was assigned to the increased molecular motion achieved at the crystalline to mesophase transition temperature.

3.7.3. Permeability of Alkali Metal Ions through Polymer/Liquid Crystal/Crown Ether Membranes

The diffusivity and permeability of alkali metal ions through a composite membrane consisting of polycarbonate/N-(4-ethoxy-benzylidene)-4'-n-butylaniline/dicyclohexyl-18-crown-6 in a weight ratio 40/60/3 were investigated and compared to a liquid membrane, poly(tetrafluoroethylene) impregnated with decanol containing the crown ether.²¹¹ The permeabilities of water and ions were measured by the osmosis method. The membrane showed, as could be expected, a higher permeability for K^+ ions than for Li^+ ions (~70 times higher). Also a membrane without crown ether showed selective transportation between K^+ and Li^+ . This result was explained on the basis of the higher hydrophobicity of the larger ion diameter of K^+ . However, the transportation of K^+ through the membrane was about 10 times higher if crown ether was included. The flux of K^+ in the composite membrane increased remarkably in the vicinity of the transition temperature from the solid to the liquid crystalline state of the liquid crystal. In the case of a membrane consisting of just polycarbonate and crown ether only a slight continuous increase of K^+ flux over the actual temperature range was observed. Based on these results it was proposed that the K^+ flux was highly dependent on

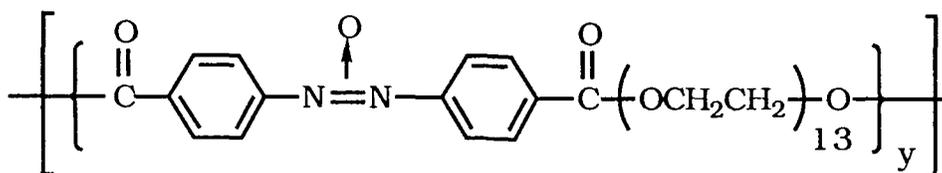
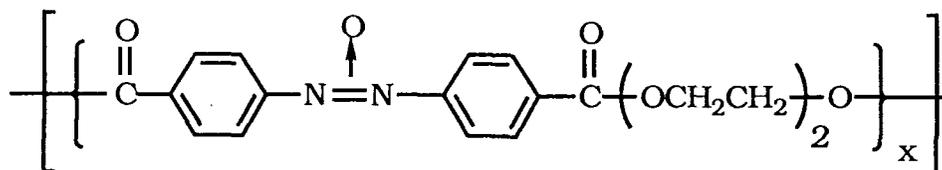
the viscosity of the liquid crystal matrix. The permeability of the composite membrane, in the isotropic state of the liquid crystal, to alkali metal ions turned out to be comparable to the permeability observed in the liquid membrane. In the liquid crystalline phase of the liquid crystals the permeability was about 3.5 times lower.

3.7.4. Photoinduced Ion Permeation in Membranes Composed of Polymer/Liquid Crystal/Azobenzene-Bridged Crown Ether

Membranes (10-100 nm thick) consisting of polyvinylchloride (PVC)/low molar mass liquid crystal/azo bridged crown ether were investigated for their photoinduced permeation of K^+ ions.^{212,213} The liquid crystals used were either 4-cyano 4'-n-pentylbiphenyl or N-(4-ethoxy-benzylidene)-4'-n-butylaniline at weight ratios of PVC/liquid crystal/azo-crown of 40/60/2.7 and 40/60/2.6, respectively. The liquid crystal compounds formed a continuous domain in the three-dimensional polymer network. The cis-azo bridged crown is able to form 1:1 sandwich complexes with metal ions and due to this it can extract K^+ ions 47.5 times as much as the trans complexes. By irradiation of the membrane with UV light on one side and visible light on the other, the authors were able to make a light-driven membrane, due to the fact that the cis-trans isomerization is possible to be induced by light (Scheme 12). The extraction of K^+ ions from a KCl solution increased markedly when the light was turned on. At the temperatures used, the liquid crystals are either in their liquid crystalline or in their isotropic state and they work as the transporting phase for the azo-crown ether molecules. The permeation of K^+ from a potassium p-toluenesulfonate solution was higher than for K^+ from a KCl solution. This was assigned to the fact that the higher hydrophobicity of the p-toluenesulfonate anion makes incorporation of the K^+ ion into the azo-crown ether in the liquid crystal phase easier.

3.7.5. Gas Permeability in Liquid Crystalline Polymers

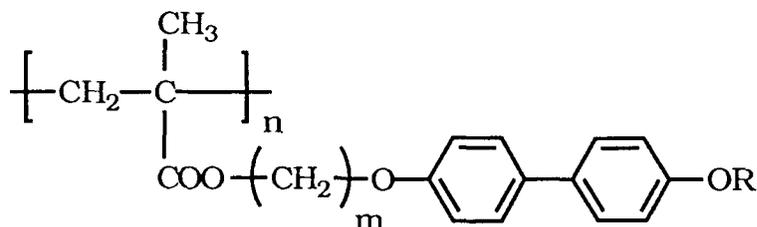
The permeability of O₂ and N₂ gases through a main-chain polymer (104) membrane and the permeability of n-C₄H₁₀ through a side-chain polymer (105) membrane were measured.²¹⁴



104

x/y = 25/75

x/y = 50/50



105

m = 6, R = -C₁₂H₂₅

m = 10, R = -C₁₂H₂₅

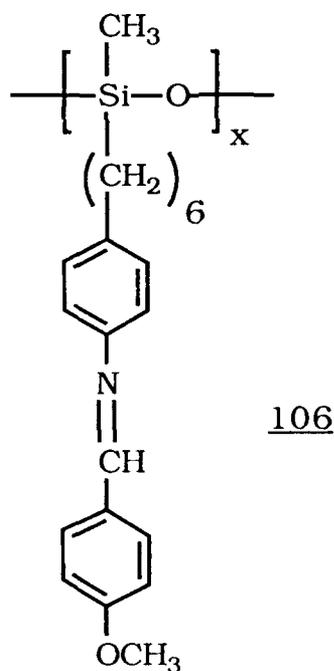
For the main-chain polymer, the magnitude of P_{O₂} and P_{N₂} increased with increasing temperature. The separation factor P_{O₂}/P_{N₂} was greater in the smectic phase than in the crystalline phase. For the side-chain polymer, P_{n-C₄H₁₀} was higher in the liquid crystalline phase due to higher molecular motion.

The gas transport properties of Vectra[®] (a random copolyester of 4-hydroxybenzoic acid and 6,2-hydroxynaphthoic acid) have been investigated.²¹⁵ The permeability coefficients at 35 °C for He, H₂, O₂, Ar, N₂ and CO₂ gases were

comparable to or smaller than those for polyacrylonitrile. This was assigned to low solubility rather than to low transport mobility.

The permeation of H₂, O₂, N₂, CH₄ and CO₂ gases through a liquid crystalline polysiloxane sandwiched between two porous polypropylene films was investigated.²¹⁶ The permeation coefficient increased markedly in the vicinity of the glass transition. However, when passing from the nematic to the isotropic state, no abrupt change of the permeability coefficient in an Arrhenius plot was observed. In addition, the separation factor (P_{O₂}/P_{N₂} and P_{CO₂}/P_{CH₄}) increased with increasing the permeability coefficient in the liquid crystalline state.

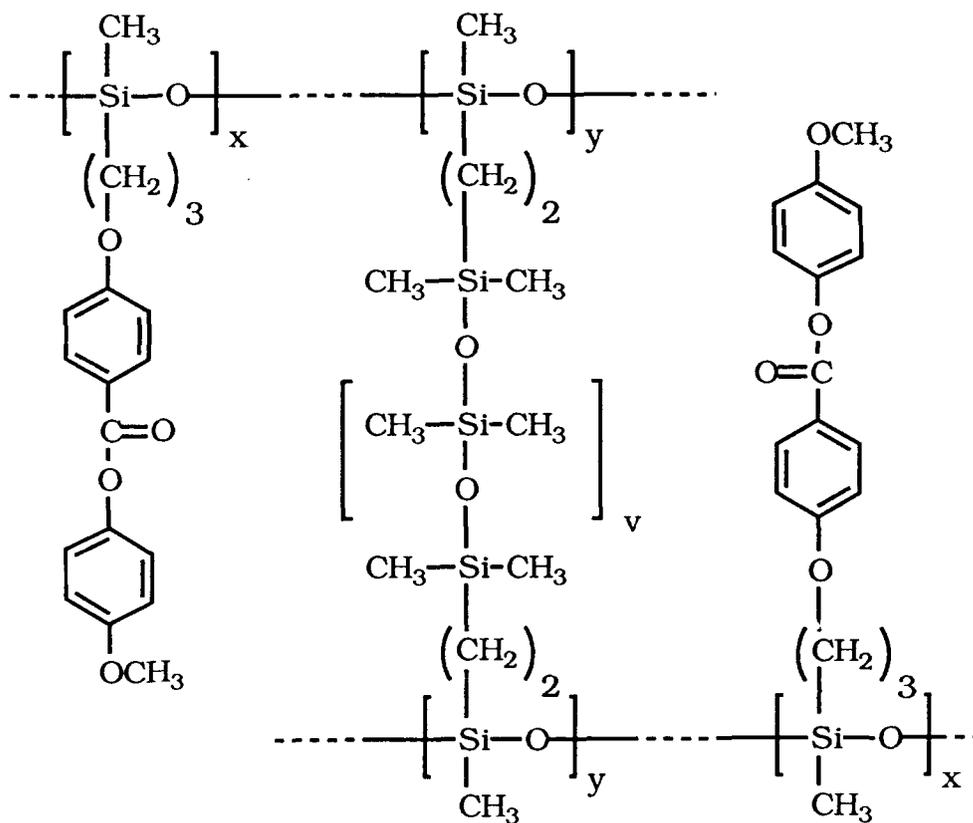
A permselective separation apparatus, which can control the separation rate, based on a side-chain liquid crystalline polymer (106) membrane and a device for controlling the permeability of the membrane by an electric field as an external force was reported.²¹⁷



A separation membrane based on 106 was placed in an electric field at 123 °C to separate O₂ from air. The O₂ separation increased with increasing the electric field intensity.

3.7.6. Diffusion through Side-Chain Liquid Crystalline Crosslinked Elastomers

The diffusion of salicylic acid through a side-chain liquid crystalline polysiloxane network elastomer (107) foil was investigated.²¹⁸



$$x + y = 60$$

$$v = 10 \text{ or } 25$$

107

Arrhenius plots of the diffusion coefficient D of salicylic acid changed their slope at the liquid crystalline to isotropic transition. The diffusivity of salicylic acid in the membrane decreased with increasing the content of mesogenic groups in the polymer and with decreasing the degree of crosslinking. The permeability through an analogous but non liquid crystalline polymer was considerably higher. Further, the solubility of salicylic acid was much higher in the liquid crystalline state than in the isotropic state, despite the lower temperature in the former state. The activation energy of diffusion in the liquid crystalline state was much higher than in the

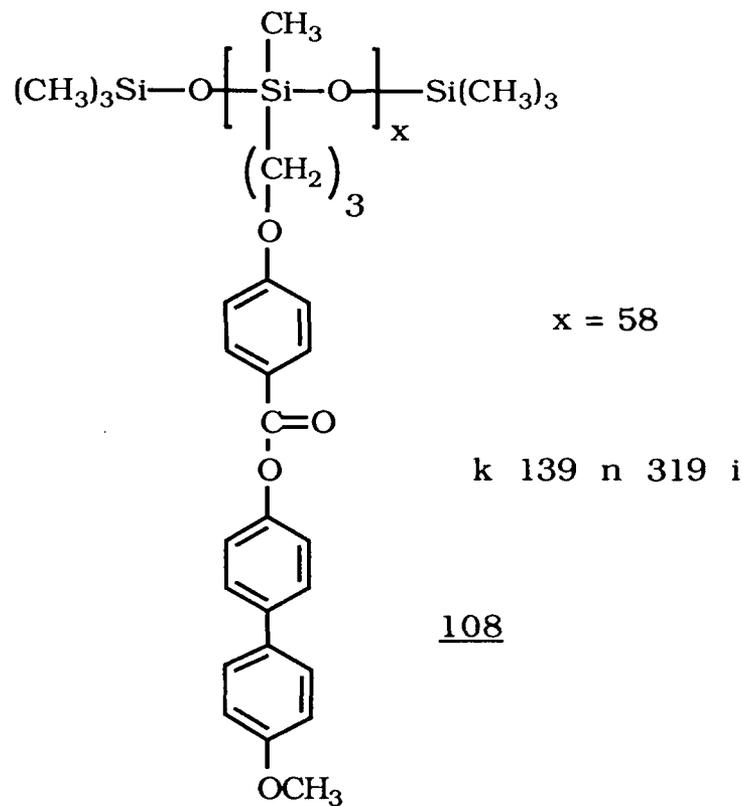
isotropic state. The activation energy increased with increasing the content of mesogenic groups also in the isotropic state. The degree of crosslinking of the polymer has a small influence on the diffusion. The diffusion coefficient was altered in a range of more than three orders of magnitude by varying the mass fraction of the mesogen from 0-0.70.

3.8 Liquid Crystals as Separation Media in Chromatography

3.8.1. Liquid Crystals as Stationary Phases in Gas Chromatography

Since the successful separation of *m*- and *p*-disubstituted benzenes by gas chromatography, using nematic *p,p'*-azoxyanisole as the stationary phase,²¹⁹ liquid crystals have gained a considerable amount of interest in this field. A large number of low molar mass liquid crystals as well as, more recently, polymer liquid crystals have been used for their good separation properties and this is documented in several comprehensive reviews.²²⁰⁻²²² Usually, the separation is based on the solute shape, giving for different solute structures different retention times. Therefore, for a given solute, the retention time will change with the phase of the liquid crystal. Due to the greater column efficiency of the nematic over the smectic state, materials like *N,N'*-bis(*p*-phenylbenzylidene)- α,α' -bis-*p*-toluidine and *N,N'*-bis(*p*-butoxybenzylidene)- α,α' -bis-*p*-toluidine, have been most frequently used. Also cholesteric compounds have been used, e.g. cholesteryl esters. In several cases they proved to be useful for separations of chiral derivatives.²²² It has been shown that the affinity of the liquid crystalline phase for the solute is always less than that of the isotropic phase.²²¹ Further, at the crystallization temperature, the partition process characteristic of the liquid crystalline phases changes to an adsorption process characteristic of the crystalline phase. Both these effects can be seen in Figure 6 for the liquid crystal *p,p'*-azoxyphenetol (PAP).

Problems with low molar mass liquid crystals, like low wetting ability to the inert gas chromatographic supports and bleeding due to high volatility at elevated temperatures initiated the use of polymer bound liquid crystals.^{223,224} A number of liquid crystalline polysiloxanes have been synthesized and used as stationary phases.



Polymer 108, being one of the most tested, has practical operating limits between 150 and 300 °C.²²⁴ The upper practical operating limit is defined by the thermal stability of the polymer and by the liquid crystalline to isotropic phase transition temperature. An interesting effect was observed for polymer 108 when the logarithm of the adjusted retention time t'_R was plotted against the reciprocal temperature for benzo[a]pyrene and benzo[e]pyrene. Instead of merging at the nematic-isotropic phase transition temperature, the two solute lines continue asymptotically, i.e. the separation is kept in the isotropic phase (Figure 7). The authors theorized that there was some residual order left in the thin film as a result of the capillary wall covering process, giving the isotropic film some anisotropic properties.^{222,224}

In addition to liquid crystalline poly(siloxane)s, also poly(acrylate)s have been synthesized and used as stationary phases, however to a much lesser extent.²²⁵

In order to achieve chromatographic resolution of enantiomers, chiral nematic poly(siloxane)s have been synthesized.²²² However, it has turned out to

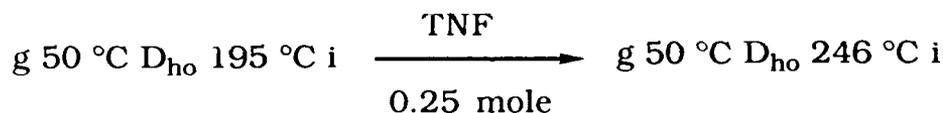
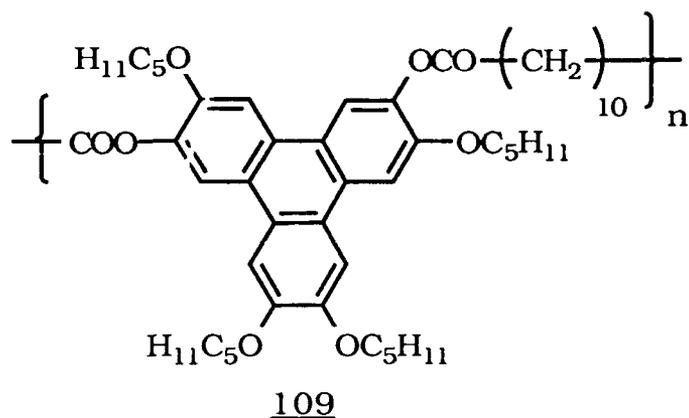
be difficult to make polymers exhibiting both chiral selectivity and mesomorphic ordering at the same time. This stems from the fact that the chiral side chains must be considerably apart from each other in order to achieve enantiomeric resolution in the separation process. The gap between the mesogenic side groups created by the insertion of non-mesogenic units in the main-chain severely restricts the formation of a mesophase.

3.8.2. Liquid Crystals in Liquid Chromatography

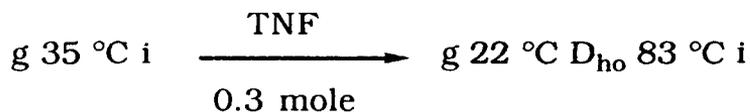
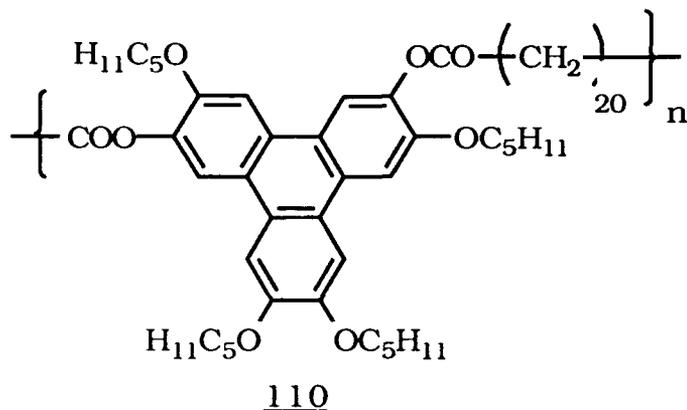
4-Ethoxybenzylidene-4'-n-butyraniline and cholesteryl oleate deposited on silica gel have been used as separation media in liquid chromatography using hexane as eluent.²²⁶ In the separation of isomers of benzene derivatives, some evidence for an increased separation was found when the liquid crystal was in its mesomorphic state.

3.9 Electron Donor-Acceptor (EDA) Complexes of Liquid Crystalline Polymers

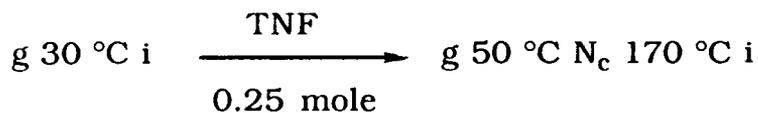
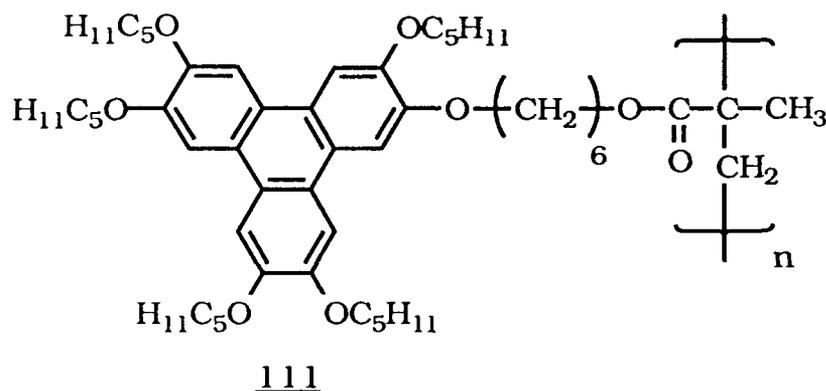
Ringsdorf et al.^{68,227} have studied the effects of doping with electron acceptor molecules on the liquid crystallinity of polymers containing donor disc-like mesogens. They found that charge transfer interactions not only increase the degree of order within the liquid crystalline phase, but also stabilize it. When the discotic main-chain polyester 109 was doped with 2,4,7-trinitrofluorenone (TNF), the width of the discotic columnar hexagonal mesophase was increased by $\sim 50^\circ\text{C}$, for molar ratios of I/TNF equal to 3/1 and 2/1.



The intermolecular spacing decreased also considerably, proportional to the amount of TNF added. The same authors doped a non-liquid crystalline main-chain polyester (110) containing disc-like mesogens and this resulted in the induction of a discotic columnar mesophase.



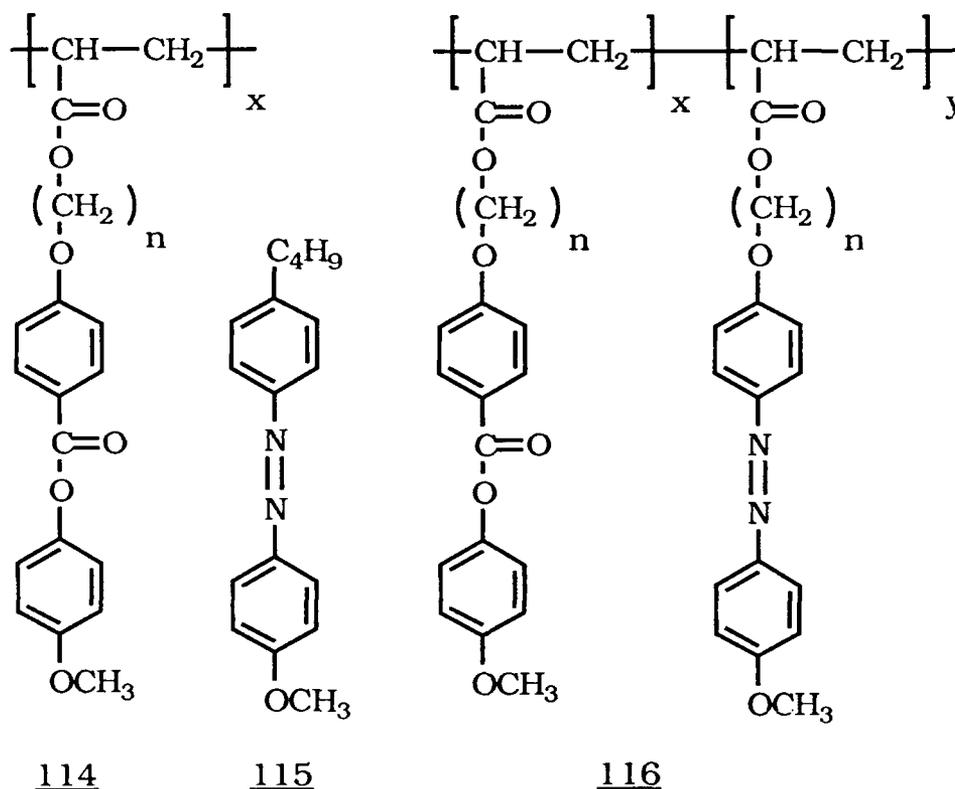
The intercolumnar spacings found were extremely large and the authors assumed that considerable amounts of TNF molecules were uncomplexed and were located in the intercolumnar spacing. Further, doping of non-liquid crystalline polymethacrylate (111) with donor disc-like groups in the side-chain resulted in the formation of a nematic columnar mesophase.



Finally, doping induced compatibility and liquid crystallinity in an incompatible mixture of non-mesogenic electron donor polymers, i.e. polymethacrylate 112 and polyester 113. The resulting discotic polymer blend exhibited a nematic columnar phase (Scheme 13).

3.10 Photochemically Induced Isothermal Phase Transitions in Polymer Liquid Crystals by Photoisomerization

Photochemically induced isothermal phase transitions by photoisomerization have been investigated in a number of polymer systems. The first system investigated was based on side-chain polyacrylates with phenyl benzoate based mesogens.²²⁸⁻²³⁰



Thin films of homopolymers 114 doped with a low molecular weight photoresponsive moiety 115 (5 mole %) or copolymers 116 with the photoresponsive group as a structural unit were irradiated with 366 nm light generated by a Ne-He laser in the nematic state. The irradiation caused the trans \rightarrow cis isomerization of the azo bond and this in turn, caused the change of the polymer from nematic to isotropic. The process was reversible upon irradiation with 525 nm light. The phase transition behavior was strongly dependent on

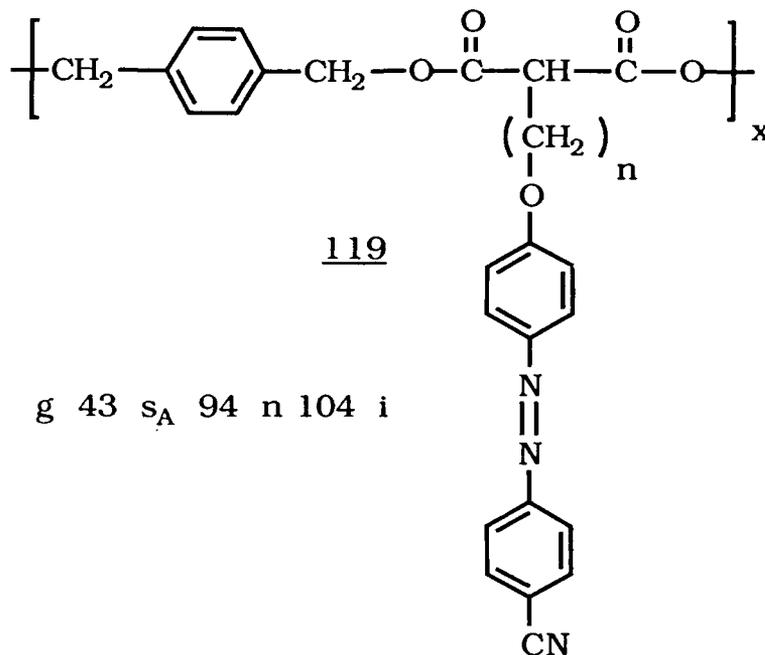
spacer length and molecular weight. Based on calorimetric and order parameter measurements by FT-IR dichroism, the photochemically induced phase transition was found to be closely related to orientational ordering of the initial state of the polymer. The nematic to isotropic phase transition took place more effectively in a system with a less ordered nematic state. It was possible to store images with a resolution of 2-4 μm in the copolymers, by irradiation of a photomask with a YAG laser.

The second system²³¹ was based on a very similar polymer but with cyanobiphenyl instead of methoxyphenyl benzoate mesogens. The effects observed in this system were similar to those described above.

A third similar system was investigated.²³² This system was based on two types of photoresistive chromophores: either azobenzene or cinnamic acid derivatives which were incorporated in poly(biphenyl vinyl ether-alt-maleic anhydride)s (Scheme 14). The azo containing copolymers (117) were irradiated with 366 nm light at various temperatures. In no case a complete phase transition was induced by the trans \rightarrow cis photoisomerization. The cinnamic acid containing copolymers (118) were irradiated at 310 nm. The irradiation resulted in photodimerization and subsequent crosslinking, however, the liquid crystalline phase did not seem to be completely disorganized.

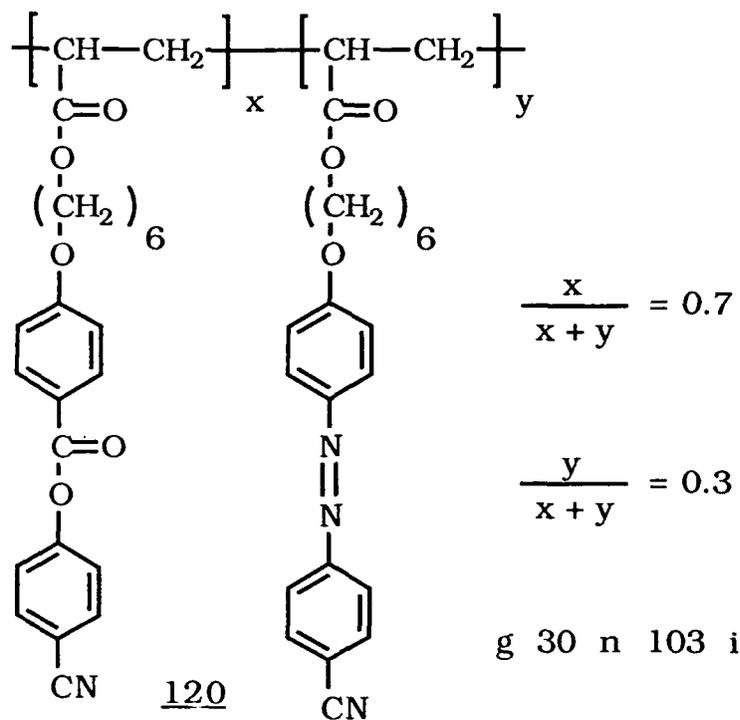
The same group investigated a low molar mass system (fourth system) based on the same principle.²³³ The system consisted of 4-butyl-4'-methoxyazobenzene (≤ 5 mole %) mixed with 4-cyano-4'-pentylbiphenyl. The same effects were observed.

Eich et al.²³⁴ investigated the photoinduced trans \rightarrow cis isomerization in a liquid crystalline polyester (119) containing azo benzene moieties as side groups.



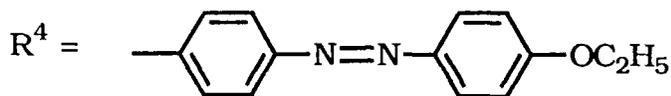
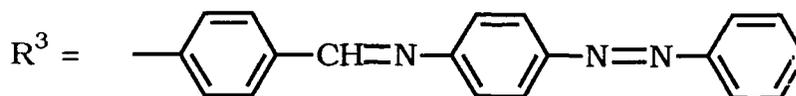
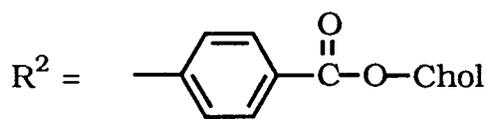
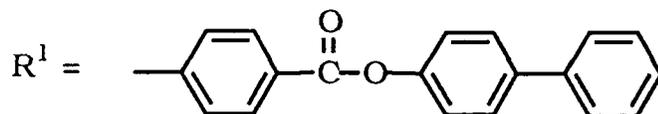
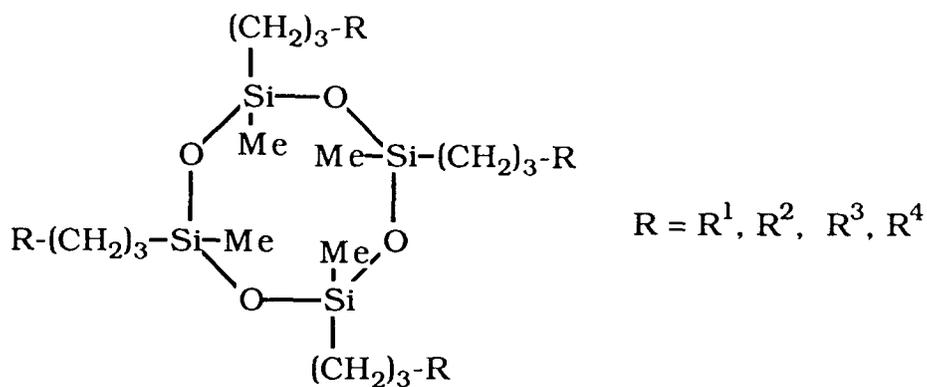
The photoisomerization process seems to be useful for applications like reversible digital and holographic data storage. A 7 μm film was oriented by an external field above T_g . The film was then irradiated at room temperature with linearly polarized light of $\lambda=514.5$ nm. The film will locally be heated to temperatures between the glass transition temperature and the isotropization temperature and a trans \rightarrow cis isomerization will take place. The orientation of the liquid crystalline phase will locally be disturbed and give rise to a local variation in birefringence. Information stored in this way does not vanish even if the azo moiety relaxes back to its trans form.

The same group^{235,236} has also investigated a second similar system (120).



These further studies concluded that despite the fact that the photo-induced trans→cis isomerization relaxes thermally back to trans, the direction of the optical axis of the sample is maintained provided that the process occurs isotropically.

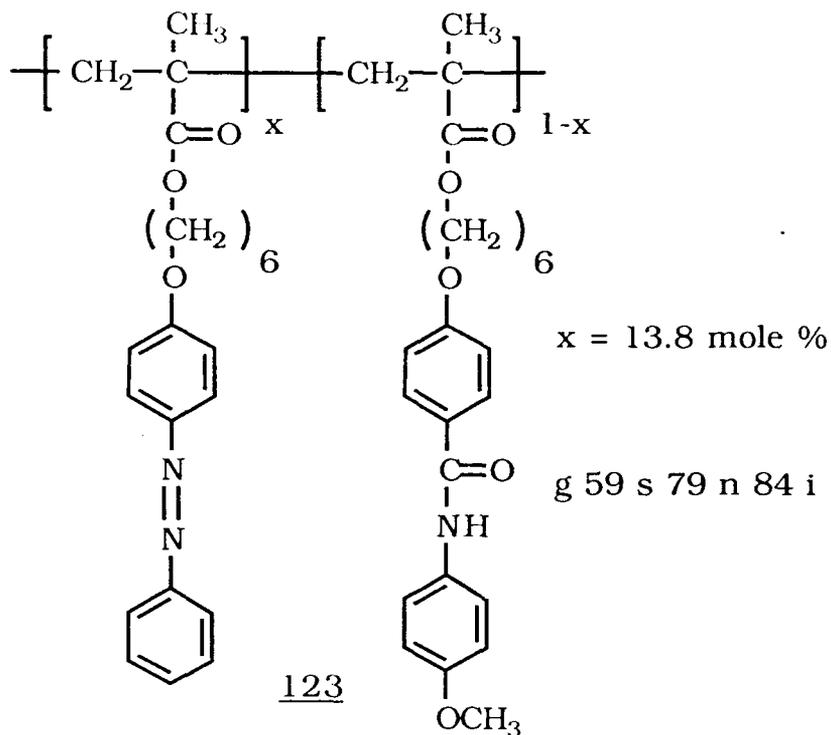
Polymers 121 and 122 were used for reversible optical data storage with holographic methods.²³⁷ The information was "frozen-in" in the glassy state of the polymer at room temperature. No change was observed for several weeks. However, the cis-azobenzene moiety relaxed back to the trans form within 5 hours.



121 : Mole ratio $R^1 : R^2 : R^3 = 2 : 1.6 : 0.4$
 $T_{g \rightarrow ch} = 50 \text{ }^\circ\text{C}$, $T_{ch \rightarrow i} = 192 \text{ }^\circ\text{C}$, $\lambda_{ref} = 790 \text{ nm}$

122 : Mole ratio $R^1 : R^2 : R^4 = 2 : 1.8 : 0.2$
 $T_{g \rightarrow ch} = 49 \text{ }^\circ\text{C}$, $T_{ch \rightarrow i} = 206 \text{ }^\circ\text{C}$, $\lambda_{ref} = 695 \text{ nm}$

The photoinduced E→Z isomerization of azochromophores was investigated in a methacrylate side-chain liquid crystalline copolymer (123) by Stumpe et al.²³⁶



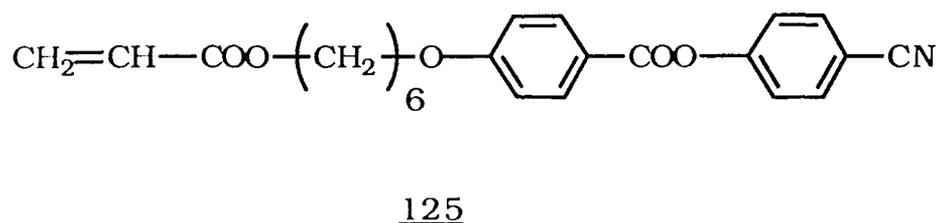
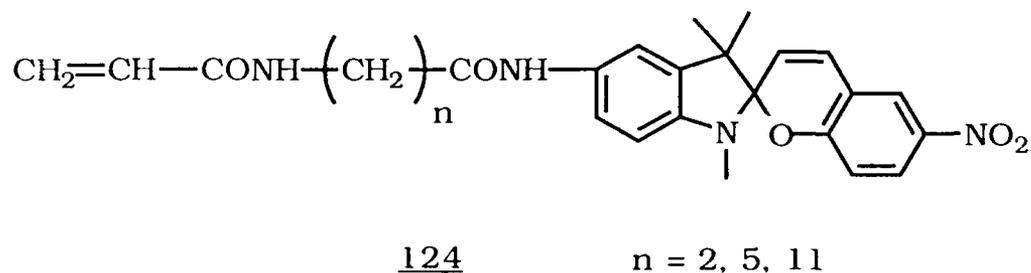
Using linearly polarized light, the E→Z photoisomerization caused macroscopic reorientation of the homeotropically oriented monodomain polymer film to a uniform planar film. Also in this case the induced dichroism and birefringence persisted after the azobenzene moieties had relaxed back to their E-isomer form.

3.11 Photochromic Liquid Crystalline Polymers

3.11.1. Reversible Systems

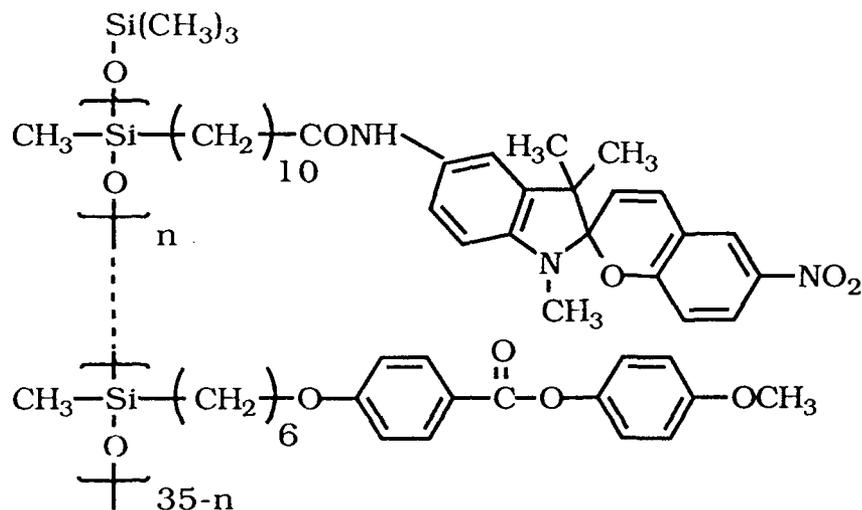
Krongauz et al.²³⁹ and Goldburt et al.²⁴⁰ have investigated the photo- and thermal-induced reversible isomerization of spiropyran groups into merocyanine dye units in side chain polymers. Atactic polymers containing spiropyran side groups undergo a "zipper" type crystallization upon isomerization due to the aggregation of the merocyanine groups into giant molecular stacks.

Cabrera et al.^{241,242} synthesized copolyacrylates of monomers 124 and 125.



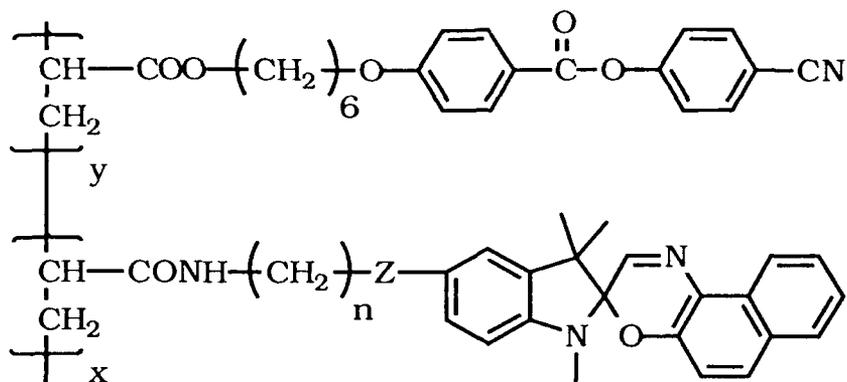
The clearing points of the liquid crystalline copolymers were lower for the higher content of spiropyran units in the copolymer. Copolymers with a high content in spiropyran did not exhibit a mesomorphic phase. Isotropic films of copolymers with low spiropyran content exhibited strong transient birefringence on shearing or other mechanical perturbation. The authors theorized that this effect was the result of macromolecular aggregation due to the thermochromic spiropyran-merocyanine transformation resulting in physical crosslinking.

The photochromic behavior of photo- and thermochromic liquid crystalline copolysiloxanes 126 has been investigated.^{243,244}

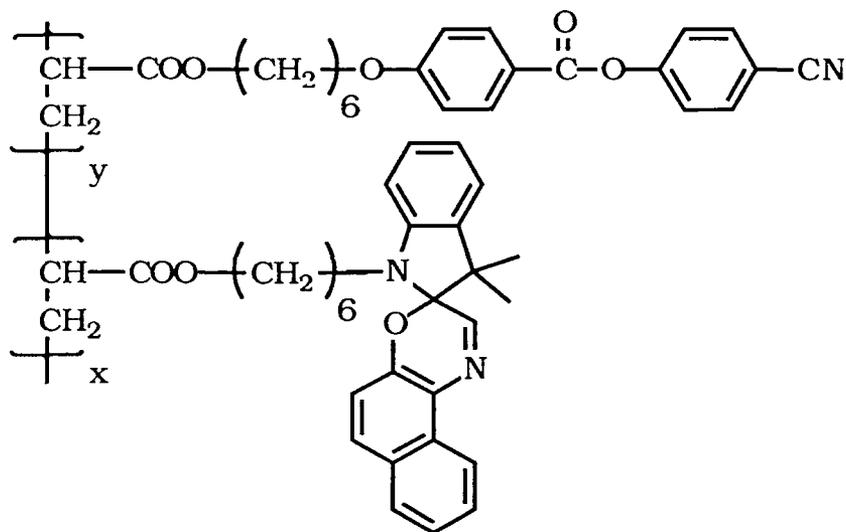


The possibility of controlling the formation of the three primary colors (red, blue, yellow) by thermo- and photochromic modulation of the spiropyran-merocyanine interconversion (Scheme 15) makes these liquid crystalline polymer systems potentially useful in imaging technology.

The photochromic behavior of the spironaphthoxazine containing copolymers (127, 128) was investigated by Yitzchaik et al.²⁴⁵



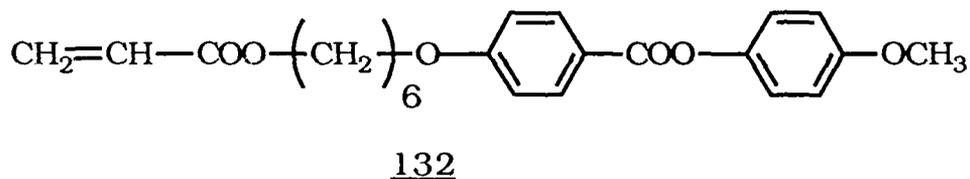
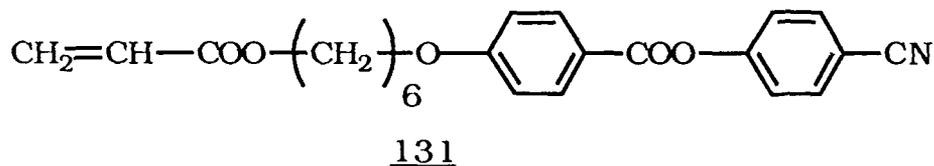
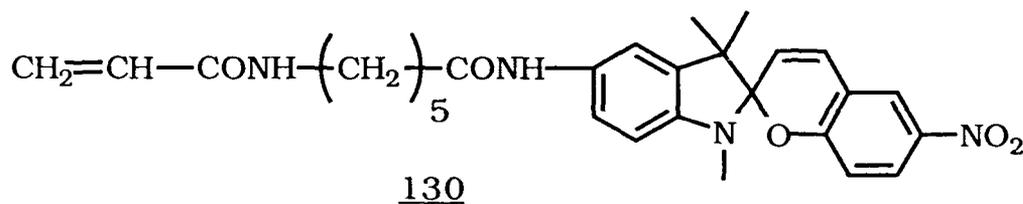
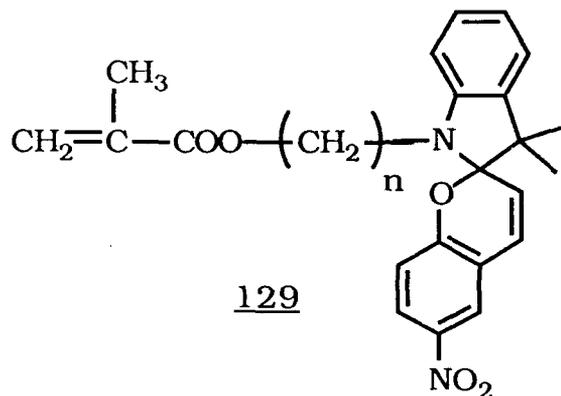
127



128

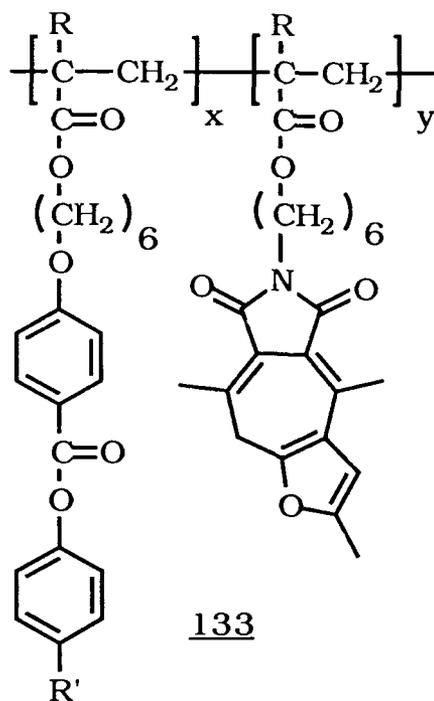
For the polyacrylates, the mesomorphic structure of a glassy film had no marked effect on the decay kinetics. The order parameter, S , was measured and was found to be very low ($S \leq 0.2$). This result made the authors to assume that separation between photochromic and mesomorphic sites took place due to structural incompatibility. From this follows that the photochromic transformations have little effect on the mesophase and vice-versa.

The same conclusions were drawn for several photochromic copolymers between monomers 129 and 130 with 131 and 132.²⁴⁶



3.11.2. Irreversible Systems

Acrylate and methacrylate fulginide monomers were copolymerized with a mesogenic phenyl benzoate monomer to give the liquid crystalline copolymers 133.²⁴⁷



$R = -H$; $R' = -CN$; $M_n \sim 5,000$

$R = -CH_3$; $R' = -OCH_3$ · $M_n \sim 14,000$

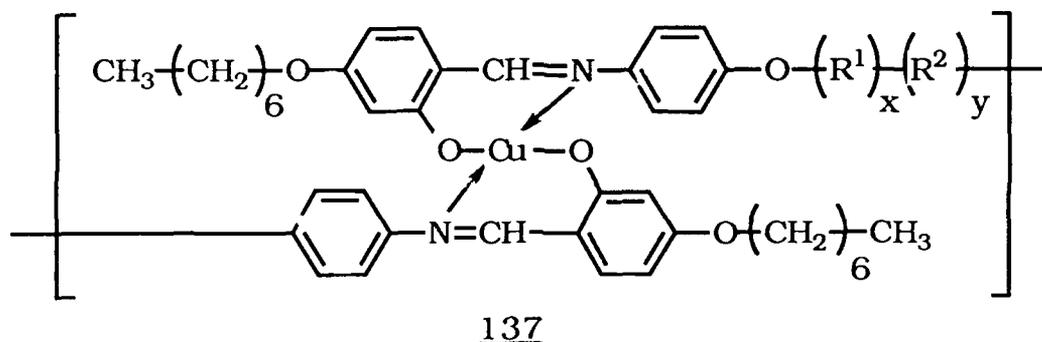
Upon irradiation of homeotropically oriented films with light of $\lambda=366$ nm, photochemical ring closure of the fulgide groups took place. The reverse reaction was achieved utilizing visible light ($\lambda>475$ nm). The photochromic effect was thermally irreversible at room temperature, in contrast to other photochromic polymers. Preliminary experiments showed that it is possible to use the films for optical data storage.

3.12 Metal Complexes in Liquid Crystalline Polymers

A recent review on metal complexes of liquid crystals and metal complexes generating liquid crystals was recently published.^{118a} Both "polymerization" and "crosslinking" reaction can be generated through complexation of various mesogenic and promesogenic monomers and polymers. Some examples are described.

A copper chloride-triethylamine coupling of the appropriate metal halide with an alkyne led to a large variety of lyotropic nematic polymers 134.²⁴⁸ Particular examples are 135 and 136 (Scheme 16).

Cu(II) containing polymers have been synthesized by coordination of the monomers with Cu(II).²⁴⁹

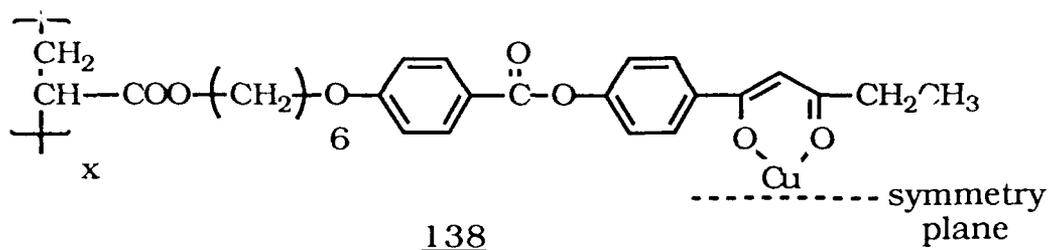


$$y = 0, 20, 50, 75, 100 \quad ; \quad y = 100 - x$$

$$x, y = \text{mole fraction } \%$$

The polymers (137) showed smectic A mesomorphism for all compositions.

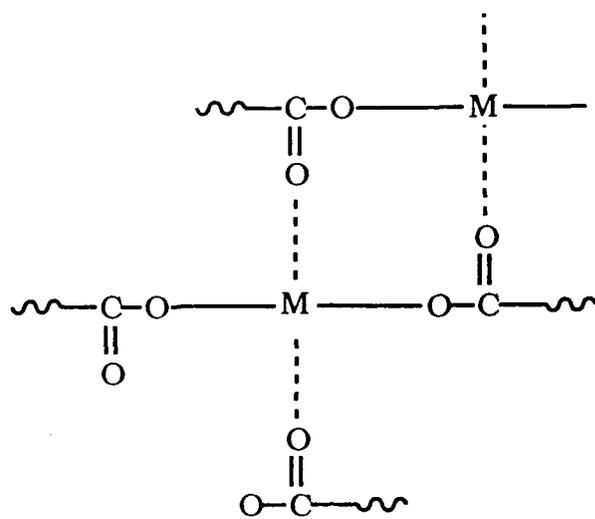
Crosslinked polyacrylates containing copper bis(β -diketonate) in the side chain (138) were synthesized by complexation of the parent soluble polymers.²⁵⁰



The mole % of copper-chelated side chain was varied between 3.9 and 92.4. The smectic behavior of the "pure" polymer was kept throughout the whole mixture range with the only possible exception being 92.4 % which showed an unidentified mesophase.

Cyanobiphenyl containing side-chain liquid crystalline acrylates have been coordinated with Pt(II) by ligand exchange reaction with dichloro bis(benzonitrile) platinum (II) to generate crosslinked polymers.²⁵¹ The mesophase of the "pure" polymer nematic or smectic (6 or 12 methylene units in the spacer) was kept in the coordinated polymer up to a Pt(II) content of about 20-25 mole %. A higher content resulted in polymers with a too high degree of crosslinking for mesophases to be formed.

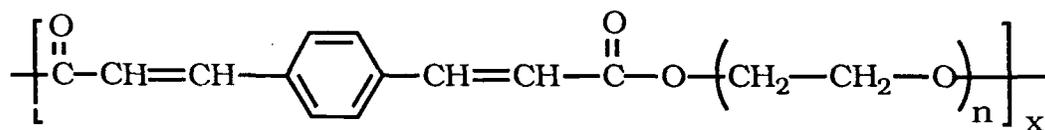
The divalent metal salts of Ba²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Cd²⁺ and p-methoxycinnamic, cinnamic, p-methoxybenzoic, and 4-n-butoxybenzoic acids were shown to produce thermotropic halatopolymers exhibiting nematic mesomorphism.²⁵² Typical melting temperatures were about 250 °C and isotropization temperatures about 270 °C. The thermal behavior was not reproducible probably due to the tendency of the divalent metal monocarboxylates to form three-dimensional networks (139) in the melt through coordination of the metal ions.



139

3.14 Excimer Formation in Liquid Crystalline Media

Excimer formation has been studied by steady-state and time-resolved fluorescence spectroscopy techniques in a liquid crystalline polymer (142) based on p-phenylenediacyrylic acid and various ethylene glycol derivatives.¹⁸⁵

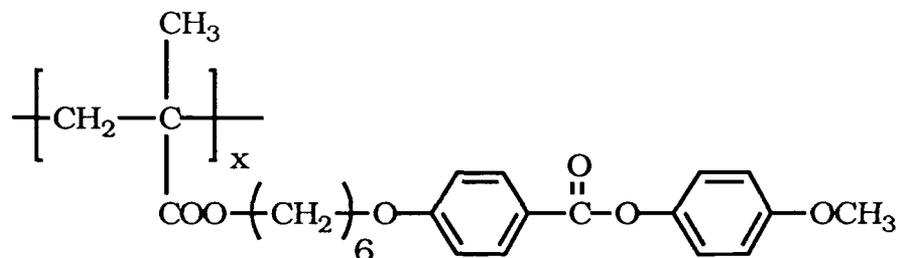


142

It was found that, like in low molar mass systems, the highest excimer formation efficiency was observed in the nematic phase.

3.15 Association in Solutions of Liquid Crystalline Polymers

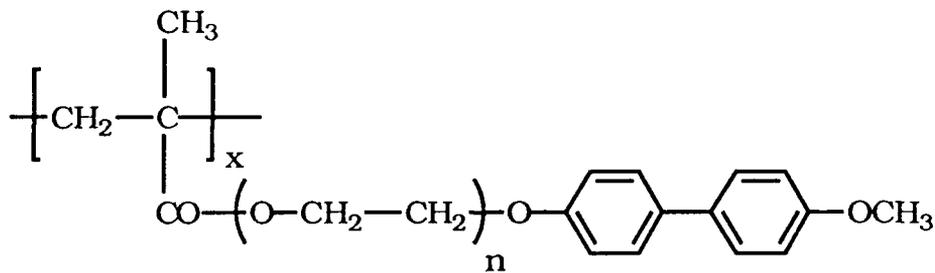
Springer and Weigelt²⁵⁴ studied the viscosity and the thermotropic properties of the liquid crystalline polymethacrylate (143).



143

Using light scattering measurements, viscosity measurements, X-ray diffraction and thermal analysis they were able to show that the polymer aggregates in solution and in the solid state the formed microcrystallites were relatively stable and could only be destroyed by melting into an isotropic phase.

The solution properties of a series of liquid crystalline methacrylates with ethylene oxide spacers (144) have been studied by the use of light scattering and size exclusion chromatography.²⁵⁵



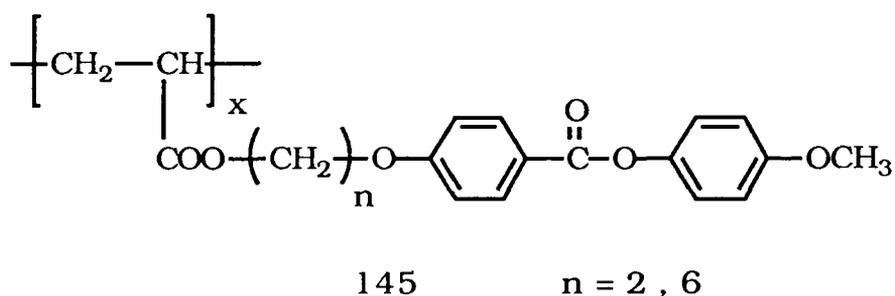
144

$n = 0 - 4$

A formation of aggregates in solution was found for homopolymers with short spacers. Since this phenomenon was not observed for copolymers having similar spacer lengths, this effect was assigned to biphenyl-biphenyl interactions.

The same polymers were also investigated for their tacticity.²⁵⁶ Although all polymers were prepared by radical polymerization in solution, the isotactic fraction decreased as the spacer length increased and at the same time the syndiotactic fraction increased (Figure 8). Apparently, the length of the spacer affects the polymerization mechanism through different degrees of biphenyl-biphenyl interactions at the growing chain end. In the case of copolymers no effect of spacer length upon the tacticity was observed except for the copolymer based on none and one ethyleneoxy unit, for which a large increase in isotactic triads and a large decrease in syndiotactic triads were observed. These results were expected since, as mentioned earlier, the possibility for biphenyl-biphenyl interactions are greatly reduced in a copolymer. The change for the copolymer having short spacers just shows that steric hindrance is important and that the homopolymer tacticity change is mainly due to steric factors.

Volinski et al.²⁵⁷ have also shown that side-chain liquid crystalline polymers interact in solution. They investigated the solution properties of a liquid crystalline acrylate side-chain polymer having methoxyphenyl benzoate moieties as mesogens (142), using light scattering measurements.



Significant differences between the values of such macromolecular parameters such as optical anisotropy δ , macromolecular diffusion coefficient D_0 and hydrodynamic radius R_H for the liquid crystalline polymers and atactic polystyrene of comparable molecular weight were observed. According to the authors, these results suggested

the formation of mesomorphic domains within the macromolecules with the dimensions of these domains being dependent on the length of the spacer.

3.16 Polymerization Induced and Enhanced Chemical Heterogeneity in Main Chain Liquid Crystalline Copolymers

Main chain liquid crystalline polymers and copolymers are synthesized by step polymerizations that are based on reversible or irreversible reactions. A polymerization reaction is reversible depending on its mechanism and on the reaction conditions used. In contrast to chain copolymerizations, step copolymerizations performed in a homogeneous phase at high conversion and with a stoichiometric ratio between comonomers always lead to copolymer compositions that are identical with the comonomer feed. Also the difference between the reactivity of various monomers used in step reactions is lower than that of the monomers used in chain reactions. This implies that the compositional heterogeneity of the copolymers obtained by step reactions is lower than that of copolymers synthesized by chain copolymerizations where copolymer composition is conversion dependent. However, again in contrast to chain copolymerizations, in step copolymerizations the copolymer's sequence distribution can be either kinetically (in irreversible copolymerizations) or thermodynamically (in reversible copolymerizations) determined.

In reversible step copolymerizations the sequence distribution is thermodynamically controlled and the copolymer microstructure is determined by redistribution reactions. The copolymer sequence distribution^{258,259} and the configuration of the structural units²⁶⁰⁻²⁶² are both determined by the type of phase (isotropic, liquid crystalline, or crystalline) in which copolymerization or the copolymer reorganization reaction is performed. Microheterogeneous copolymerization reactions complicate the control of the copolymer's microstructure since the comonomers' concentration around the growing chain is determined by the miscibility and/or the association between the growing chain and the monomers. The concept that the growing active chain can control its own environment during

copolymerization was explained on the basis of the "bootstrap" model and its implications were recently reviewed.²⁶³ Some of the most recent examples of "bootstrap effects" were observed in the radical copolymerization of macromonomers,²⁶⁴ in the synthesis of block copolymers from immiscible amorphous segments,^{265,266} and in the synthesis of ternary copolymers from monomers that can give rise to amorphous and liquid crystalline structural units by reversible copolymerization reactions.²⁶⁷

Copolymerization reactions performed in bulk are frequently used in the preparation of liquid crystalline polyesters. The starting monomers lead to isomorphous melts, nevertheless above a certain conversion this reversible reaction is performed in the liquid crystalline phase. A heterogeneous composition is generated both by the different reactivity of the monomers and by the polydispersity of the polymers. This heterogeneous composition generates a microphase separated reaction mixture which at a given temperature contains isotropic, liquid crystalline, and crystalline phases. Each of these phases generates a polymer homologous series of copolymers which have both different compositions and for the same composition a different sequence distribution. The sequence distribution is determined by the phase in which the copolymer is generated i.e., isotropic, liquid crystalline, or crystalline. This microheterogeneous copolyesterification reaction enhances the chemical heterogeneity of the resulted copolymers. Both the polydispersity and the chemical heterogeneity of liquid crystalline copolymers are responsible for the biphasic or even multiphasic nature of liquid crystalline copolyesters.^{46,268-272} The chemical heterogeneity of liquid crystalline copolymers is reduced in the case of azeotropic irreversible copolymerizations.^{273,274}

3.17 Molecular Recognition Directed Self-Assembly of Supramolecular Liquid Crystals

The molecular recognition of complementary components leads to systems able to self-assemble or self-organize i.e., systems capable to generate spontaneously a well defined supramolecular architecture from their components under a well-defined set of conditions.²⁷⁵

Although self-assembly is a well recognized process in biological systems,^{276,277} the general concept of self-assembly of synthetic molecules by molecular recognition of complementary components, received a revived interest only after it was integrated by Lehn in the new field of supramolecular chemistry.^{275,278,279}

Several examples in which molecular recognition induced the association of complementary nonmesomorphic components into a low molar mass or polymer supramolecular liquid crystal are described below.

The principles of formation of a mesogenic supramolecule from two complementary components is outlined in Scheme 17. The particular example used by Lehn et al.²⁸⁰ to generate a supramolecular mesogenic group which exhibits hexagonal columnar mesophases is by formation of an array of three parallel hydrogen bonds between groups of uracil and 2,6-diaminopyridine type as those depicted in Scheme 17.

The transplant of the same concept to the generation of a supramolecular liquid crystalline polymer is outlined in Scheme 18.²⁸¹ The complementary moieties used TU₂ and TP₂ are uracil (U) and 2,6-diacylamino-pyridine (P) groups connected through tartaric acid esters (T). The tartaric acid (T) unit provides in addition, the opportunity to investigate the effect of changes in chirality on the species formed. Thus the components LP₂, LU₂, DP₂, MP₂ and MU₂ are derived from L(+), D(-) and meso (M) tartaric acid respectively. Although all monomers

(LP₂, LU₂, DP₂, MP₂ and MU₂) are only crystalline, the corresponding supramolecular "polymers" obtained through hydrogen bonding (LP₂ + LU₂, DP₂ + LU₂ and MP₂ and MU₂) exhibit hexagonal columnar mesophases. These hexagonal columnar mesophases are generated from cylindrical helical suprastructures.²⁸¹

An additional example of supramolecular liquid crystalline polymer obtained through the hydrogen bonding of nonmesomorphic monomers was recently reported.²⁸²

Examples in which a mesophase was generated through the hydrogen bonding dimerization of carboxylic acid derivatives were available in the classic literature on liquid crystals and were extensively reviewed.^{6,283} New and interesting examples on the generation of nonsymmetrical liquid crystalline dimers,²⁸⁴ twin dimer²⁸⁵ and side chain liquid crystalline polymers²⁸⁶ by specific hydrogen bonding "reactions" continue to be reported (Scheme 19).

Recently, a new approach to molecular recognition directed self-assembly of a liquid crystalline supramolecular structure by a mechanism which resembles that of self-assembly of tobacco mosaic virus (TMV) was reported.²⁸⁷ The self-assembly mechanism of TMV is outlined in Scheme 20.²⁷⁷ The synthetic approach can be summarized as follows. A flexible polymer backbone containing tapered side groups self-organizes the side groups into a column which surrounds the polymer backbone (Scheme 21). These polymers exhibit thermotropic hexagonal columnar mesophases (Scheme 22). Although the number of chains penetrating through the center of the column is not yet known and requires further research (Scheme 21), it seems that this self-assembling system is complementary to those elaborated by Lehn et al.^{280,281} In the model elaborated by Lehn et al.^{280,281} the complementary pairs are self-organized through hydrogen bonding type interactions, while in the last case²⁸⁷ only the shape of tapered side groups is responsible for the generation of a polymeric column.

3.18 Miscible Blends of Rigid Rod-like Polymers with Flexible Polymers (Molecular Composites) via Ionic Interactions

As was discussed in more details in Chapter 1.3 for thermodynamic reasons,²⁸⁸ liquid crystalline polymers or any other kind of rigid rod-like polymers are not miscible with flexible polymers. A homogeneous dispersion at the molecular level of a rod-like polymer into a flexible polymer has the potential to lead to a molecular composite.²⁸⁹ In fact most pairs of flexible polymers are not miscible either.²⁹⁰ However, in the case of flexible polymer chains a miscible blend can be accomplished by using specific interactions between the two polymers and thus generate an exothermal mixing. Hydrogen bonding,²⁹⁰ electron donor-acceptor²⁹¹ and ionic²⁹² interactions were used for this purpose. Recently, ionic interactions generated by mixing solutions of poly(p-phenylene benzobisthiazole) and poly(sodium 2-acrylamido-2-methyl propane sulfonate) in methanesulfonic acid were used to prepare a homogeneous mixture of a rigid rod-like polymer with a flexible polymer.²⁹³ Upon dissolution of poly(p-phenylene benzobisthiazole) in methanesulfonic acid, onium ions were generated by the protonation of the nitrogen atoms in the thiazole groups. At the same time, free poly(2-acrylamido-2-methyl propanesulfonic acid) was obtained by the dissolution of poly(sodium 2-acrylamido-2-methyl propane sulfonate) in methanesulfonic acid. The ionic interactions between the onium and sulfonate groups are responsible for the generation of this miscible blend (Scheme 23).

Rigid rod-like helical poly(γ -methyl L-glutamate) and poly(γ -ethyl L-glutamate) form homogeneous blends with flexible poly(p-vinylphenol) due to hydrogen bonding between the phenol groups of the flexible polymer and the ester groups of the rigid polymers.²⁹⁴ At the same time, poly(γ -benzyl L-glutamate) form a microphase separated system.

3.19 Liquid Crystals Containing Crown Ethers and Polypodants

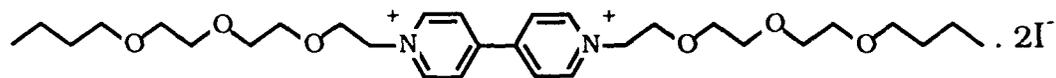
Mesomorphic host-guest complexes of low molecular weight and polymer liquid crystals containing macroheterocyclic ligands and polypodants provide a novel approach to self-assembled systems which combine selective recognition with external regulation.^{275,295, 296}

The first examples of thermotropic low molar mass liquid crystals refer to a series of disc-like amide derivatives of macroheterocyclic cycloamines that exhibit columnar mesophases.²⁹⁷⁻²⁹⁹ Rod-like liquid crystalline compounds containing a benzocrown ether moiety were also reported.³⁰⁰⁻³⁰²

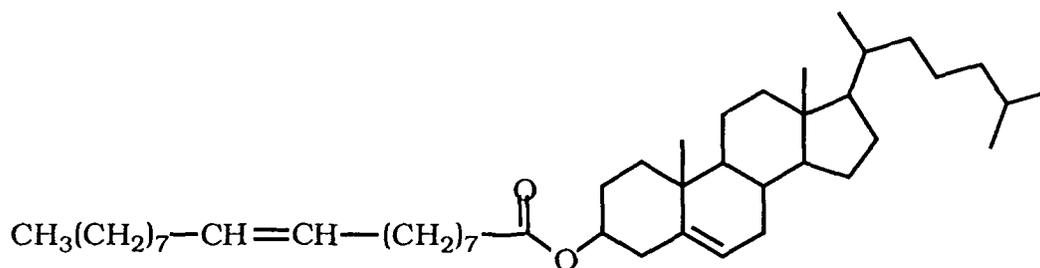
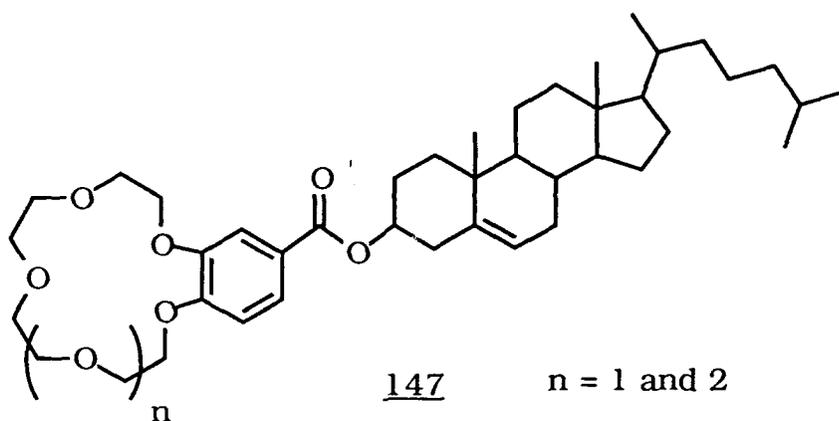
Three basic architectures can be considered for liquid crystalline polymers containing crown ethers (Scheme 24): main chain liquid crystalline polymers containing crown ethers in the main chain of the polymer and side chain liquid crystalline polymers containing crown ethers either in the mesogenic group or in the main chain. Alternatively, the same series of polymers with polypodants instead of crown ethers can be considered.

Main chain liquid crystalline polyamides and polyethers containing crown ethers were reported.^{303,304} A variety of side chain liquid crystalline polymers containing the crown-ether group at one end of the mesogenic unit were designed.³⁰⁴⁻³¹⁰ Side chain liquid crystalline polymers containing crown ethers in the main chain were synthesized by living cationic cyclopolymerization and cyclocopolymerization of 1,2-bis(2-ethenyloxyethoxy)benzene derivatives containing mesogenic side groups.^{311,312}

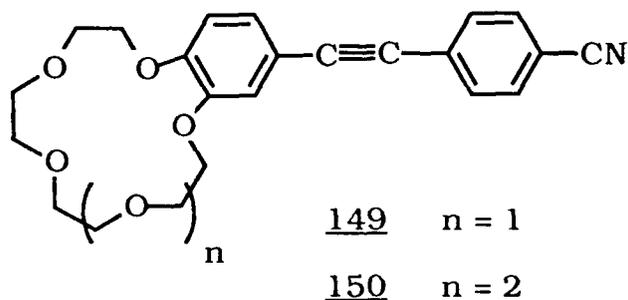
The use of oligooxyethylenic spacers in main chain³¹³ and side chain liquid crystalline polymers^{67,314,315} leads to liquid crystalline polypodants. Both main chain³¹³ and side chain^{316,317} liquid crystalline polypodants dissolve large amounts of alkali metal salts, and the resulting liquid crystalline polyelectrolytes are ionic conductors.³¹⁷

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The liquid crystalline viologen iodide containing oligooxyethylene groups (146) acquired a 10^5 -fold enhancement in electric conductivity when an electric stimulus of 1-30 V was applied at 110 °C i.e., when 146 was in its liquid crystalline phase.³¹⁸

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A composite membrane based on an amorphous polymer and a mixture containing the cholesteryl oleates 147 and the cholesteryl oleate 148 exhibits a cholesteric liquid crystalline phase at room temperature and was claimed to behave as a biological membrane which functions based on the channel mechanism.^{319,320}



Fluorescence and absorption studies of the cation-binding behavior of crowned liquid crystals in solution and in the nematic phase were performed.³⁰² For example, the 4'-[(p'-cyanobiphenyl)ethynyl]benzo crown ethers 149 and 150 not only display a nematic liquid crystalline phase but also show very strong fluorescence, both in solution and in the liquid crystalline state. Compound 150 exhibits a bathochromic shift in fluorescence and a hypsochromic shift in absorption with increasing solvent polarity. The addition of alkali metal cations produced hypsochromic changes in both the fluorescence and absorption of 150. Both 149 and 150 complex alkali metal cations selectively in the nematic phase, and the cation-binding ability is comparable to that found in methanol solution.

The helical pitch of cholesteric liquid crystals 147 is sensitively affected not only by the bound metal cations, but also by that of the counteranions.³²¹ These results demonstrate the possible application of cholesteric liquid crystals containing crown ethers as host-guest sensory systems, since the change of the helical pitch can be detected spectroscopically. In this respect, this system can be regarded as providing the transformation of chemical signals into physical signals. The potential use of such systems to "recognize" optically active guest molecules through a diastereomeric interaction was also demonstrated.³²¹

These very few examples of liquid crystalline host-guest systems have demonstrated that they have the potential to generate phase-dependent operating systems which provide novel approaches to systems that combine a highly selective recognition coupled with external thermal, electromagnetic and mechanical regulation.

Conclusions

The original idea behind this chapter was to discuss polymerizations in liquid crystalline media. It was very clear even from the introductory subchapters that organization, miscibility, phase diagrams and reactions of any kind including polymerizations in low molar mass and polymeric liquid crystals are all determined by physical and chemical specific interactions, or in other words by molecular recognition. Therefore, it was almost impossible to separate molecular chemistry (i.e., the chemistry of the covalent bond) from supramolecular chemistry (i.e., the chemistry of intermolecular bond which is determined by specific interactions).²⁷⁵ Since the field of liquid crystals is the one which pioneered the research on self-organized systems it seems to be the richest so far in examples on various aspects of supramolecular chemistry. We did not intend to provide a comprehensive coverage of the literature but only a survey of the past few years, and at the same time we tried as much as possible to select representative examples. Although most of the topics enumerated are presently understood only in a qualitative way, we believe that many of them provide unique approaches to the problem discussed. A series of topics can and should borrow knowledge from neighboring fields. For example, topochemical reactions in liquid crystalline media has many things to learn from topochemical polymerizations in crystalline media,³²² while epitaxial polymerization on liquid crystalline phases or epitaxial polymerization of liquid crystalline monomers on an ordered surface should do it too.³²³ Finally, we hope that this short review will bring the interest of more traditional scientists interested in various aspects of the chemistry and physics of liquid, amorphous and crystalline phases to the field of liquid crystalline phases, *which nature uses so much and we know so little about.*

Acknowledgments

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Table I. Some properties of lyotropic systems composed of an amphiphile and water

Suggested structural arrangement						
% Water ^a (approximate range)	0	5-22-50	23-40	34-80	30-99.9	Greater than 99.9
Physical state	Crystalline	Liquid crystalline, lamellar	Liquid crystalline, face-centered cubic	Liquid crystalline, hexagonal compact	Micellar solution	Solution
Gross character	Opaque solid	Clear, fluid, moderately viscous	Clear, brittle, very viscous	Clear, viscous	Clear, fluid	Clear, fluid
Freedom of movement	None	2 directions	Possibly none	1 direction	No restrictions	No restrictions
Microscopic properties (crossed nicols)	Birefringent	Neat soap texture	Isotropic with angular bubbles	Middle soap texture	Isotropic with round bubbles	Isotropic
X-Ray data	Ring pattern 3-6 Å	Diffuse halo at about 4.5 Å	Diffuse halo at about 4.5 Å	Diffuse halo at about 4.5 Å		
Structural order	3 dimensions	1 dimension	3 dimensions	2 dimensions	None	None

^a The different percentages of water show that different amphiphiles require different amounts of water. For soaps, the lamellar structure generally occurs between 5 and 22% water; with some lipophiles the water may be as high as 50%. The cubic structure generally occurs between 23 and 40%.

Table II. Product yields (%) from reaction of 7 and 8 in isotropic and liquid crystalline solvents at 200 °C

solvent	<u>9</u> + <u>10b</u>	<u>10a</u>	<u>11</u>
benzene (i)	48	31	14
cholestanyl benzoate (i)	43	31	19
cholesteryl-4-chlorobenzoate (ch)	43	31	17
S1544 (s _B)	29	25	32
	28	24	39

i = isotropic; ch = cholesteric; s_B = smectic B

Table III. Irradiation of 12 in isotropic, liquid-crystalline and crystalline phases

Solvent/ Phase	Irradiation ^a Temperature (°C)	% Conversion (±1%)	Relative Product Ratios ^b		
			<u>13</u>	<u>14</u>	<u>16</u>
n-hexane (5 x 10 ⁻⁴ M)	25-26	31	28	72	c
n-hexane (1.54 x 10 ⁻² M)	25-26	41	24	76	c
n-hexadecane (1.2 x 10 ⁻² M)	25-26	27	29	71	c
n-hexadecane (2.5 x 10 ⁻² M)	166.5	19	29	71	c
cholesteric liquid crystal (neat) ^d	166.5	4-6	c	14	86
crystal (neat) ^d	27-29	6	c	23	77

^a ± 0.5 °C

^b Cinnamic acid was not analyzed for in these experiments. Its yield is presumed to be that of 16

^c None detected

^d Average of at least 5 different experiments.

Table IV. Irradiation of 17-19 in n-butyl stearate

Cinnamate	% cinnamate (by wt)	phase (T, ± 0.5 °C)	% conversion ^a ($\pm 5\%$)	trans/cis ^b (± 0.1)	H-T/H-H ^c
<u>17</u>	20	isotropic (32)	41	4.3	2.5 (± 0.9)
		smectic (18)	12	9.1	8.0 (± 0.6)
		solid (8)	9	15.7	8.0 (± 0.6)
<u>18</u>	20	isotropic (32)	40	2.4	3.3 (± 0.7)
		smectic (18)	12	10.6	>20 ^d
		solid (8)	12	11.0	>20 ^d
<u>19</u>	10	isotropic (32)	53	0.9	e
		smectic (18)	37	1.9	9.4 (± 0.2)

^a % conversions are for disappearance of the trans isomer and use ω -undecylenyl benzophenone-4-carboxylate as standard

^b trans/cis isomer ratios corrected for detector response assuming $\epsilon_{\text{trans}} = 2.25 \epsilon_{\text{cis}}$ at 254 nm

^c (H-T)/(H-H) dimer ratios reported assuming $\epsilon_{\text{H-T}} = \epsilon_{\text{H-H}}$ at 254 nm

^d estimated limit of HPLC detection

^e None detected

Table V. Summary of thermal and rate parameters for the polymerization of monomer 43.

T(°C)	Monomer <u>43</u> Phase	H _{max} (mV)	T _{max} (s)
31.6	Crystalline	0.19	>20
43.7	Crystalline	0.44	7.6
52.1	Smectic	2.85	5.8
57.8	Cholesteric	3.32	5.5
125.0	Isotropic	0.99	5.8

Table VI. Polymerization of vinyl ether monomers (49-52).

Monomer	Initiation	Polymerization temperature (°C)	Conversion (%)	M _n (g/mole)	M _w /M _n
<u>49</u>	thermal	92	90	83,300	1.87
<u>49</u>	thermal	100	98	60,100	2.09
<u>52</u>	thermal	120	99	41,500	2.11
<u>49</u>	photo	80	98	37,200	1.95
<u>50</u>	photo	80	98	21,200	2.01

Table VII. Thermal transitions of polymers 73.

Sample	T _{s-lc} * (°C)	T _{lc-i} (°C)
uncrosslinked	149	195
90 % styrene	95	225
30 % styrene	125	245

* solid to liquid crystalline transition

Table VIII. Phase transitions and compositions of crosslinked polymers 85a-g

Polymer	x	y	z ^{a)}	m	Phase transition temperatures ^{b)} in K
<u>85a</u>	0	108	12	3	g 273 n 335 i
<u>85b</u>	60	54	6	3	g 264 n 285 i
<u>85c</u>	60	51	9	3	g 266 n 286 i
<u>85d</u>	60	48	12	3	g 263 n 283 i
<u>85e</u>	60	48	12	4	g 258 s 305 i
<u>85f</u>	60	48	12	6	g 253 s 332 i
<u>85g</u>	60	48	12	3	g 261 n ⁺ 308 i

a) $(x + y + z = 120)$

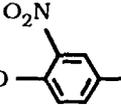
b) g = glassy; i = isotropic; n = nematic; n⁺ = cholesteric (chiral nematic); s = smectic

Table IX. Phase transitions of uncrosslinked (89a-91a) and crosslinked (89b-91b) chiral combined polymers

No.	Y	X ₁	X ₂	R	Molecular weight (GPC)	Cross-linker (mol %)	Phase transitions (°C) ^a
<u>89a</u>	-N=N-	-N=N-	-N=N-	R ₁	60,000	---	c 109 s _C * 124 n* 149 i
<u>89b</u>	-N=N-	-N=N-	-N=N-	R ₁	---	10	c 99 s _C * 114 n* 141 i
<u>90a</u>	-N(O)=N-	-N=N-	-N=N-	R ₁	47,000	---	g 24 s _C * 115 n* 149 i
<u>90b</u>	-N(O)=N-	-N=N-	-N=N-	R ₁	---	10	g 25 s _C * 110 n* 147 i
<u>91a</u>	-N(O)=N-	---	---	R ₂	17,000	---	g 20 s _C * 124 n* 130 i
<u>91b</u>	-N(O)=N-	---	---	R ₂	---	20	g 19 s _C * 110 n* 123 i

a) c = crystalline or highly ordered smectic phase; g = glassy; s_C* = chiral smectic C; n* = cholesteric phase; i = isotropic melt

Table X. Phase transitions of the chiral homopolymers 92-94

No.	R	X	Y	Phase transitions ^a (°C)
<u>92</u>	C ₂ H ₅ -*CH(CH ₃)*CH(Cl)-	---	---	c 114 s _x 121 s _C * 133 i
<u>93</u>	C ₂ H ₅ -*CH(CH ₃)*CH(Cl)-	---	-N(O)=N-	s _y 84 s _A 112 i
<u>94</u>	C ₆ H ₁₃ *CH(CH ₃)-O- 	-N(O)=N-	---	g 18 s _A 103 n* 130 i

a) c = crystalline; s_x or s_y = highly ordered smectic phase; g = glassy; s_C* = chiral smectic C; s_A = smectic A; n* = cholesteric phase; i = isotropic melt

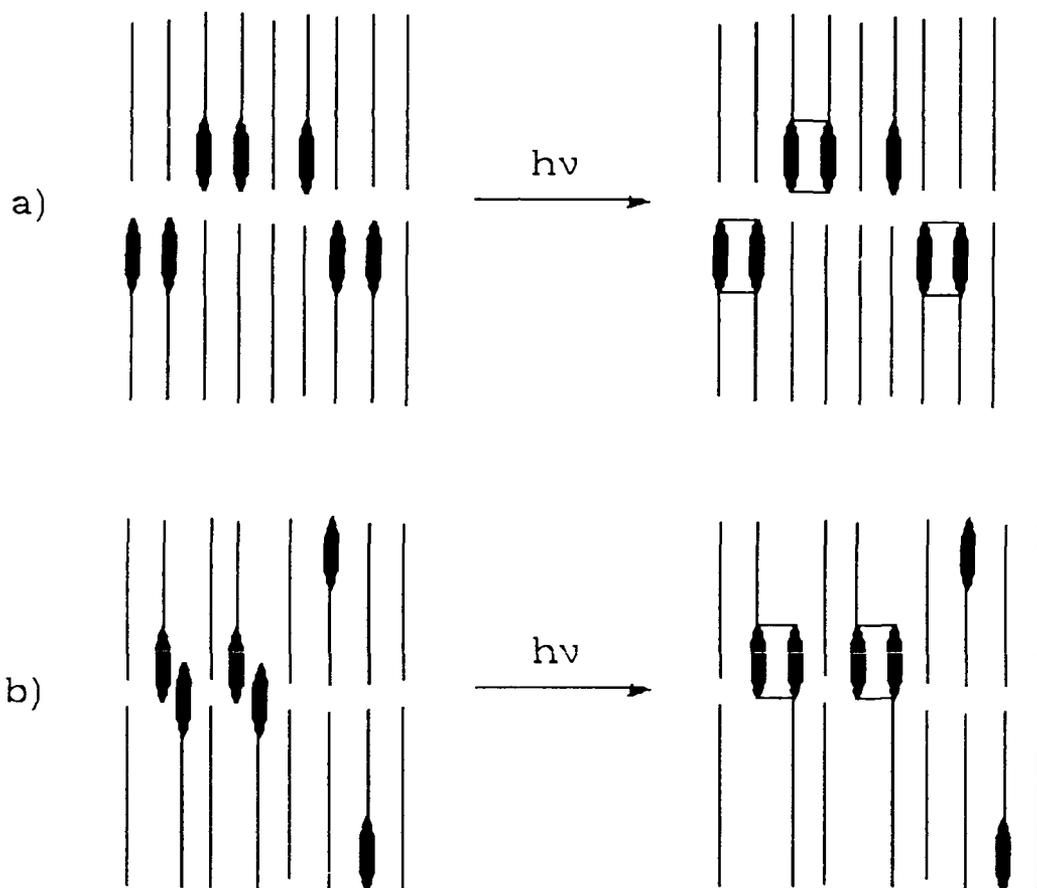
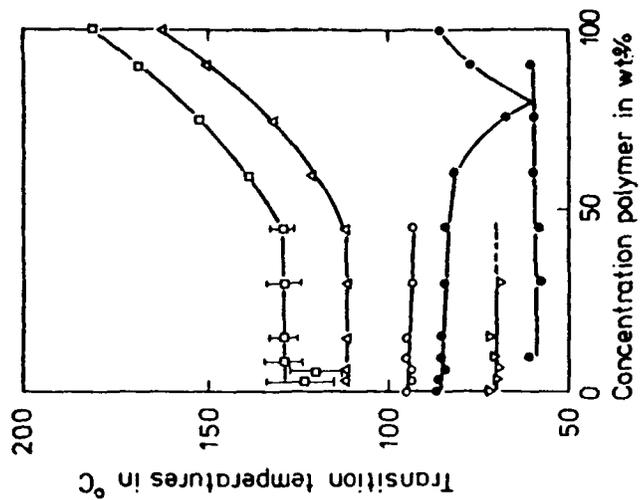


Figure 1.

a) Representation of orientations of cinnamate molecules within the smectic or the crystalline phase of n-butyl stearate assuming that the solute molecules are constrained within one layer. Without diffusion, the cinnamate pairs must give head-to-head dimers upon irradiation.

b) Representation of orientations of cinnamate molecules within the smectic or the crystalline phase of n-butyl stearate assuming that the solute molecules are aligned antiparallel and are partially overlapping. The pairs must give head-to-tail dimers without diffusion.

Figure 2. Thermal transition temperatures (measured by a combination of DSC and polarization microscopy) versus composition of blends of monomer 46/polymer. (O) and (▽): the nematic-isotropic and the nematic-smectic transitions in the polymer-poor areas, (Δ) and (□): the smectic-nematic and the nematic-isotropic transitions in the polymer-rich areas, (●): crystalline melting temperatures



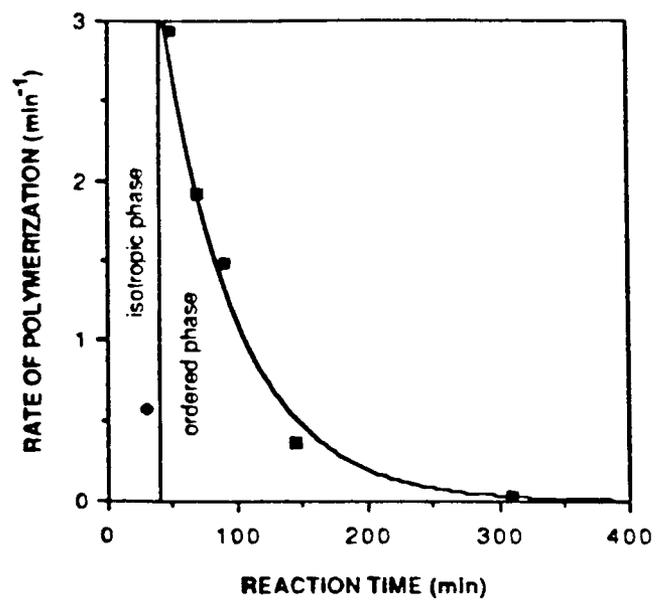
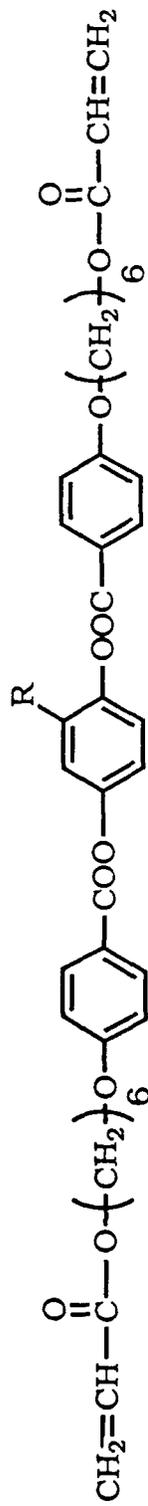
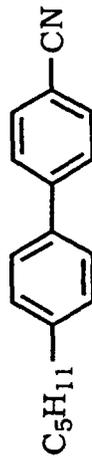


Figure 3. Plot of the rate of polymerization versus the reaction time for the synthesis of 15 wt % final concentration of poly(p-phenylene benzobisthiazole) in polyphosphoric acid



83

R = H, CH₃



84

Figure 4. Photopolymerization of mixtures of diacrylates 83 and low molar mass liquid crystal 84 in the nematic state leads to anisotropic gels

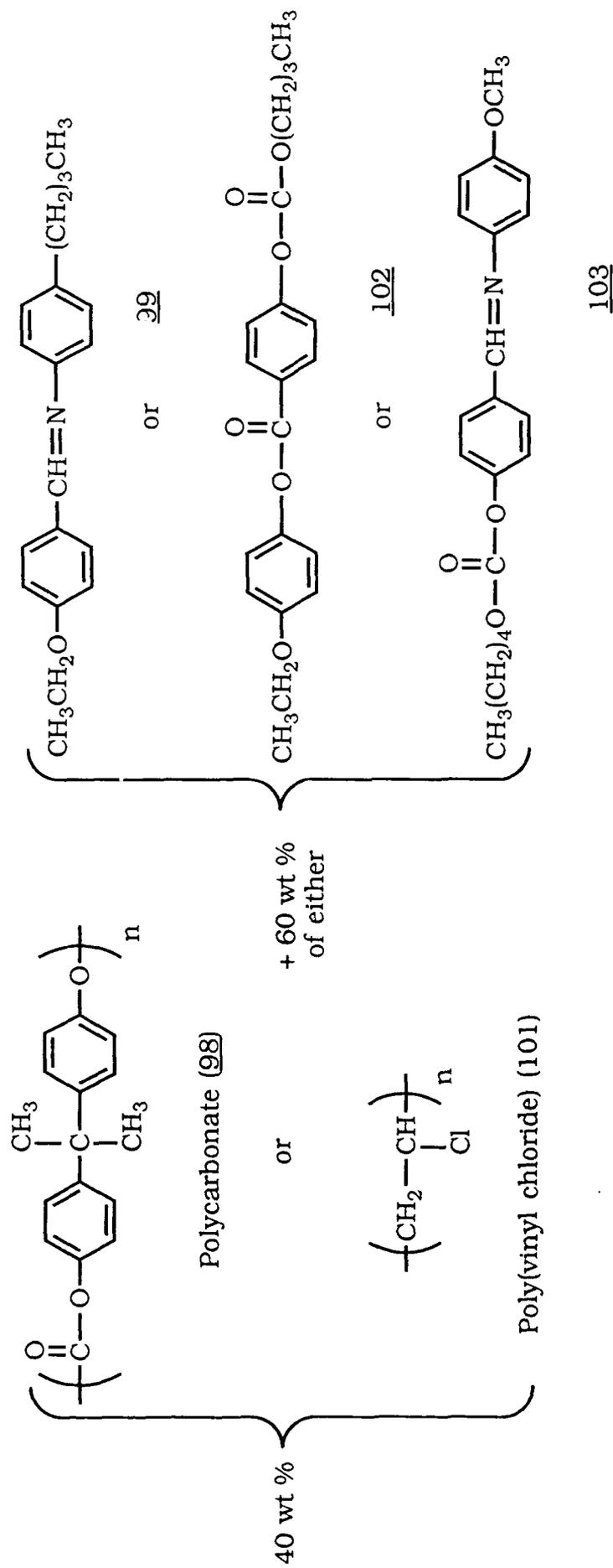


Figure 5. Compositions of membranes of polycarbonate or polyvinylchloride and low molar mass liquid crystals

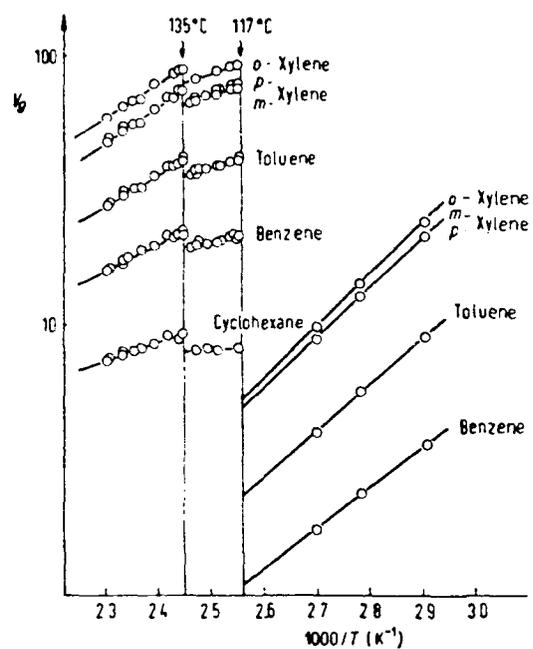


Figure 6. Specific retention volumes, V_g , versus reciprocal absolute temperature $1000T^{-1}$, for various solutes, in the solid, nematic, and isotropic phases of p,p' -azoxyphenetol (PAP).

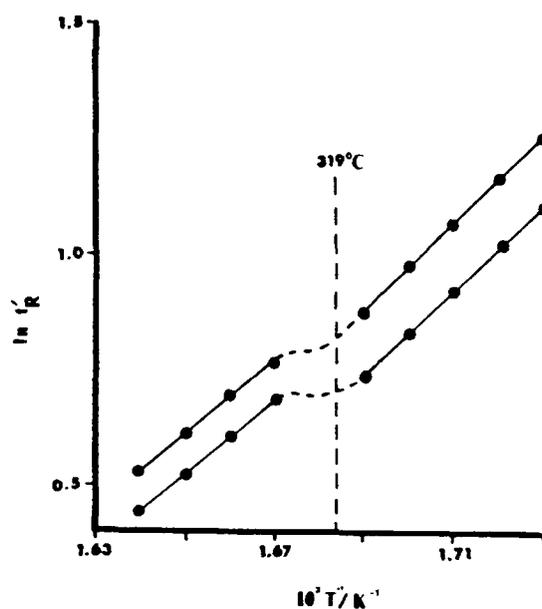


Figure 7. Plots of $\log \tau'_p$ versus reciprocal absolute temperature T^{-1} for benzo[a]pyrene (upper curve) and benzo[e]pyrene (lower curve) solutes with a stationary phase of 108. The isotropization transition temperature of polymer 108 is indicated by the dashed line ($319^\circ C$)

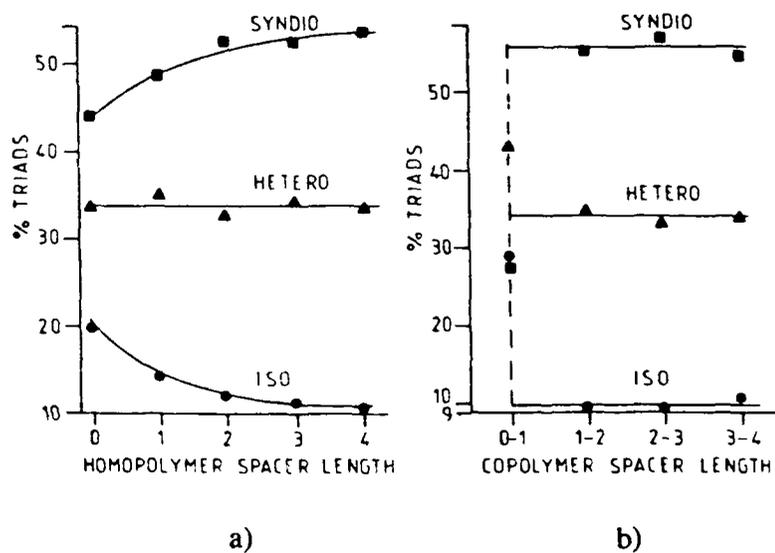
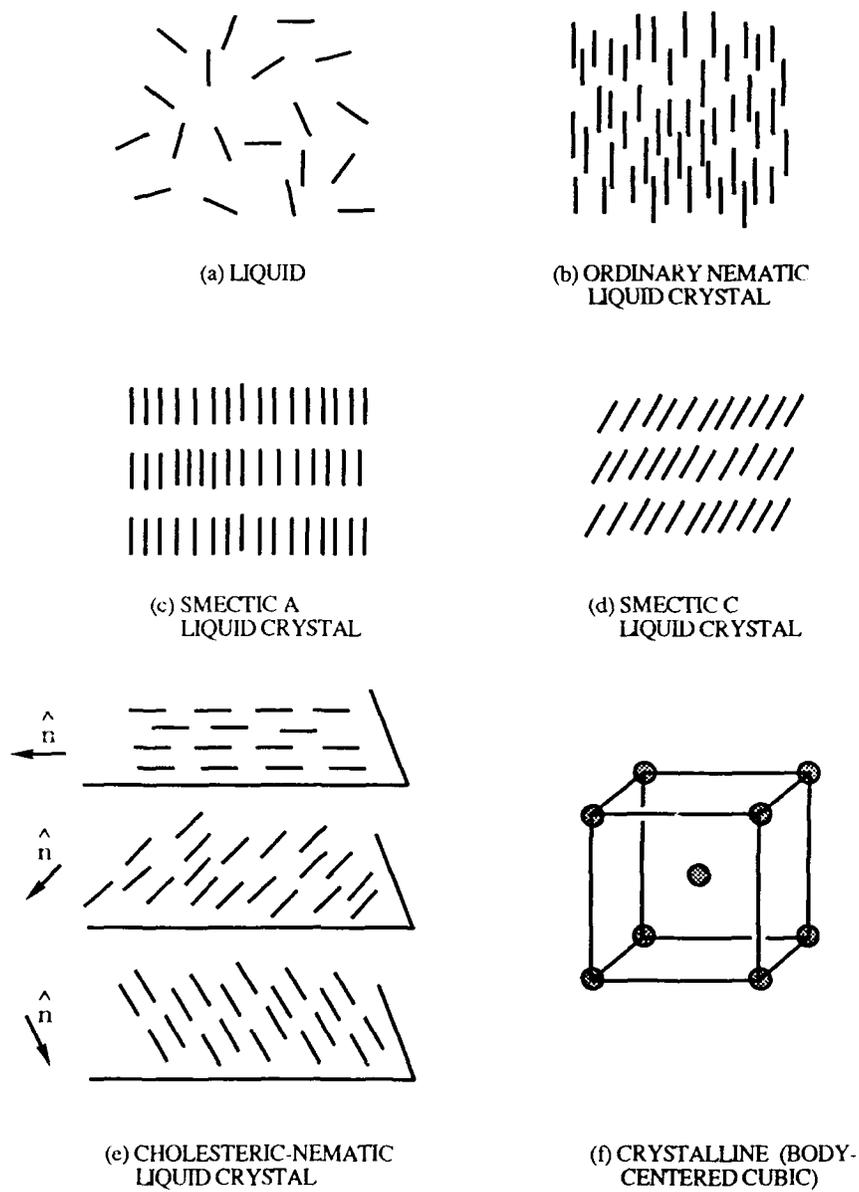


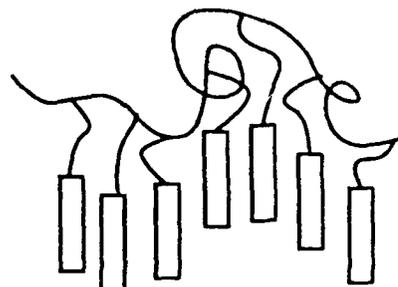
Figure 8. a) Triad tacticity versus spacer length (number of ethylene oxide units) for methacrylate homopolymers; b) Triad tacticity versus spacer length (average number of ethylene oxide units) for methacrylate copolymers



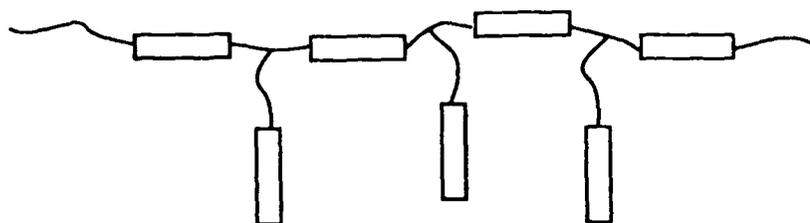
Scheme 1. Schematic representation of the molecular arrangement in the (a) isotropic phase; (b) nematic phase; (c) smectic A phase; (d) smectic C phase; (e) cholesteric or chiral nematic phase; (f) crystalline state (dots represent molecules)



MAIN CHAIN LIQUID CRYSTAL
POLYMERS

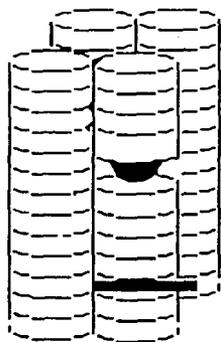
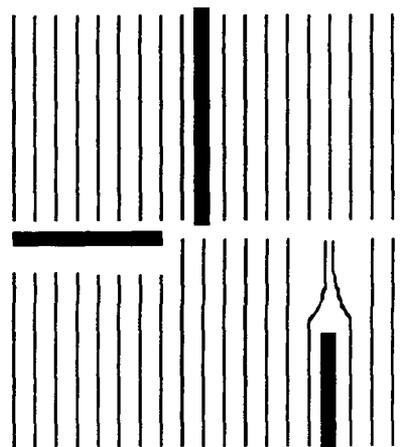
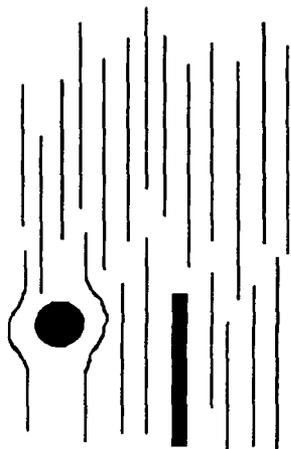


SIDE CHAIN LIQUID CRYSTAL
POLYMERS

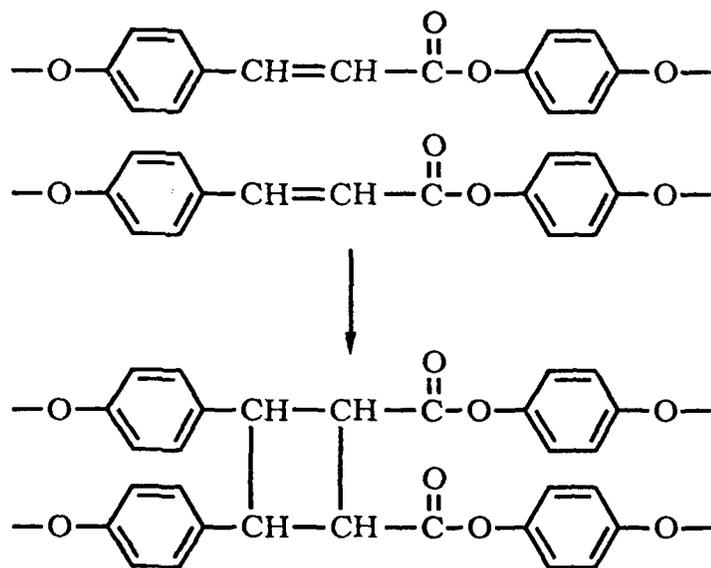


COMBINED LIQUID CRYSTAL
POLYMERS

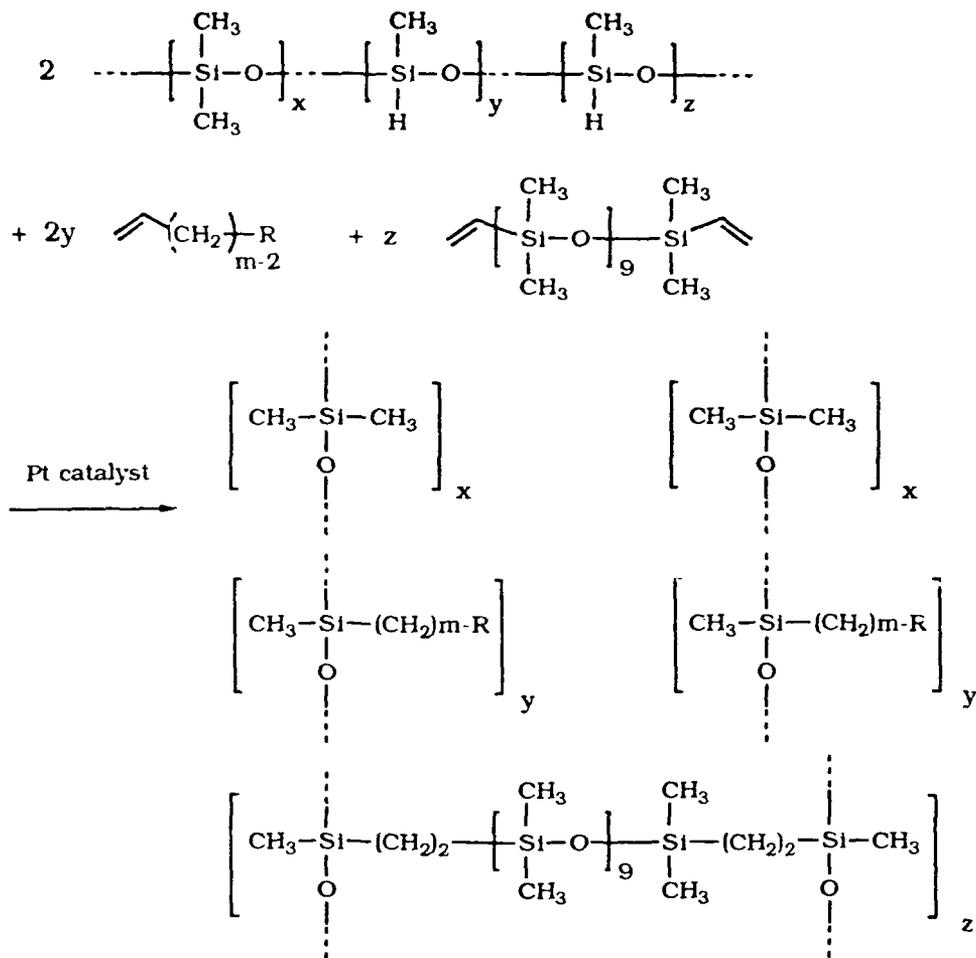
Scheme 2. Schematic representation of main chain, side chain, and combined liquid crystal polymers



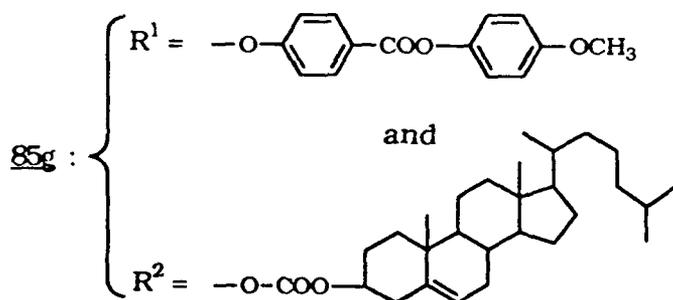
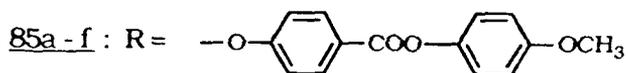
Scheme 3. Schematic representation of solubilization sites of rod-like and sphere-like solute molecules (filled shapes) in isotropic and anisotropic phases



Scheme 4. Crosslinking by cyclobutane ring formation in main chain liquid crystalline polymers containing cinnamate moieties



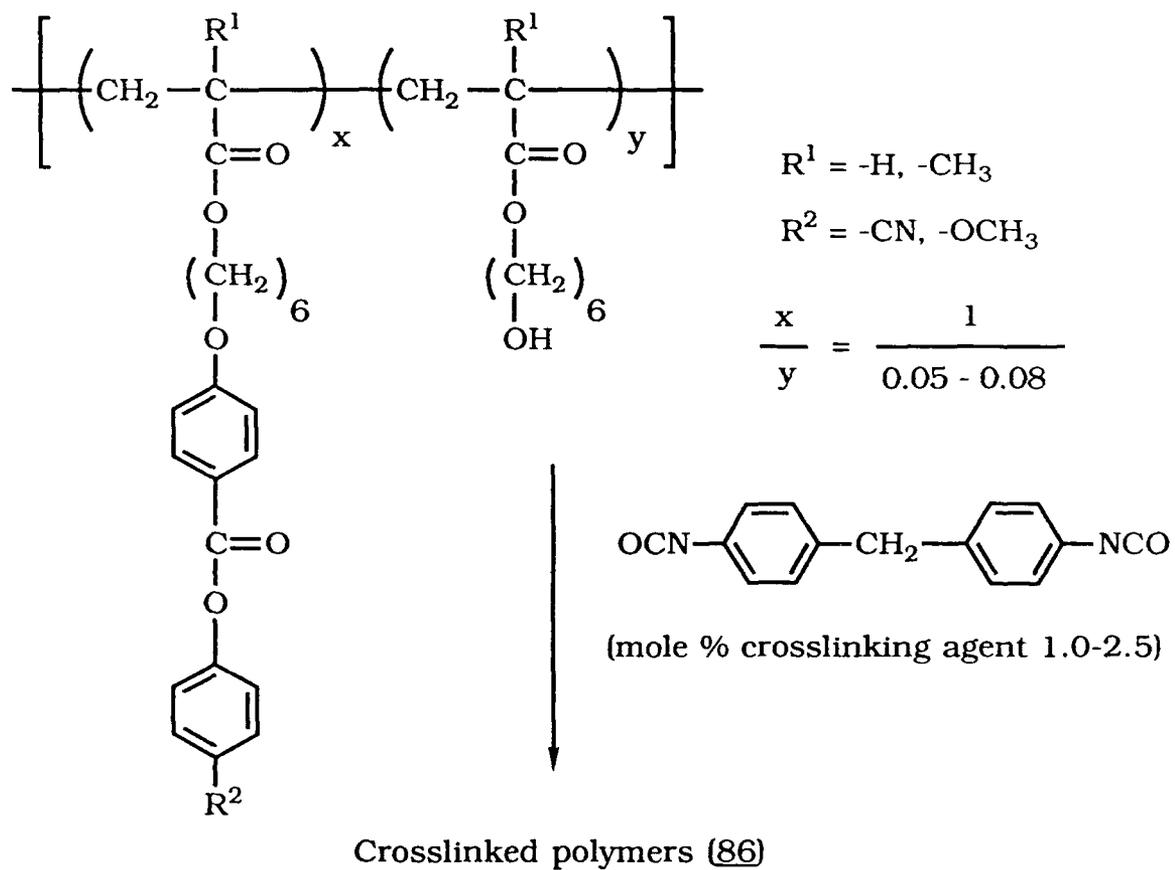
85a-g



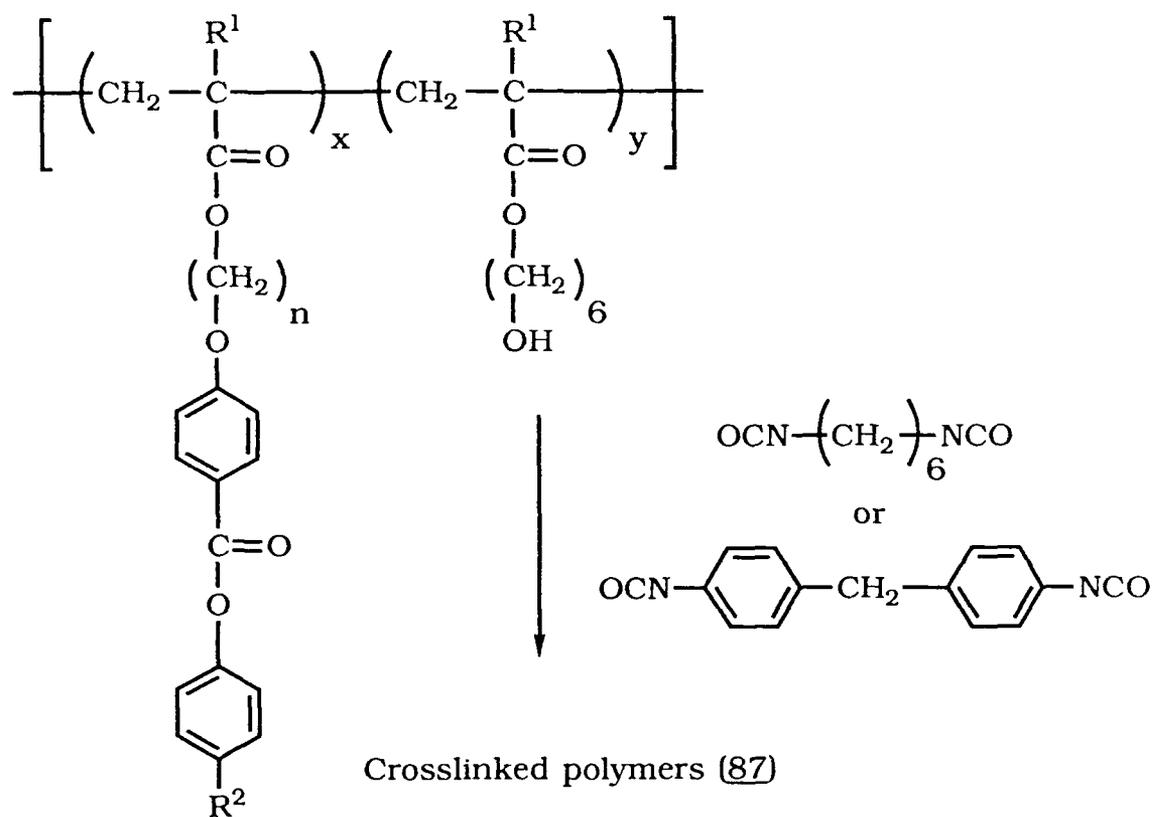
	x	y	z	m
85a	0	108	12	3
85b	60	54	6	3
85c	60	51	9	3
85d	60	48	12	3
85e	60	48	12	4
85f	60	48	12	6
85g	60	48	12	3

mole ratio $\text{R}^1/\text{R}^2 = 0.89/0.11$

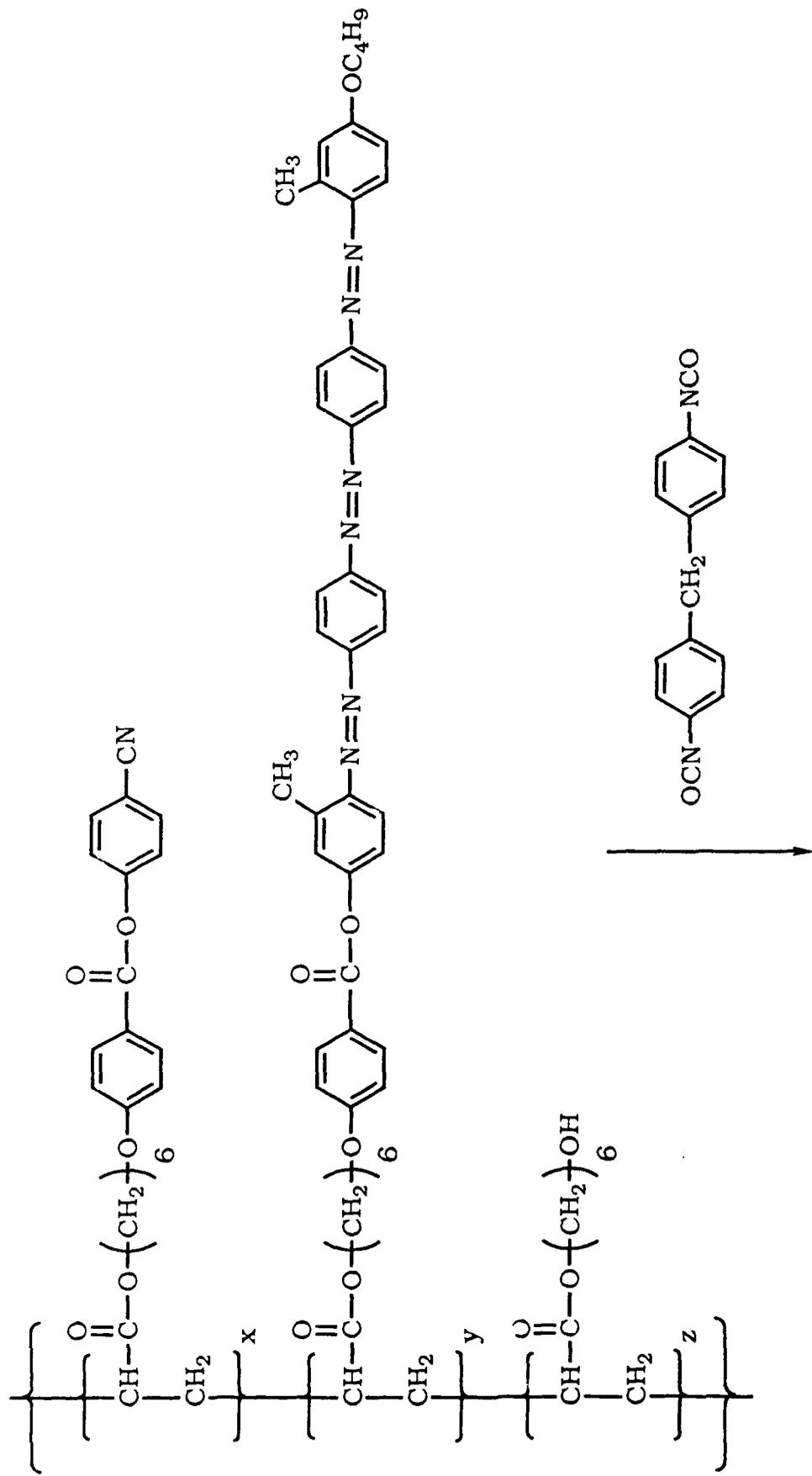
Scheme 5. Liquid crystalline elastomers (**85a-g**) based on liquid crystalline polysiloxanes



Scheme 6. Synthesis of liquid crystalline elastomers **86** by reaction of functionalized side chain liquid crystalline copolymers with 4,4'-diphenylmethane diisocyanate

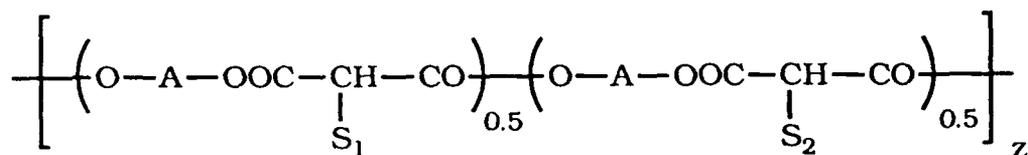


Scheme 7. Synthesis of liquid crystalline elastomers **87** by reaction of functionalized side chain liquid crystalline copolymers with hexamethylene or 4,4'-diphenylmethane diisocyanate

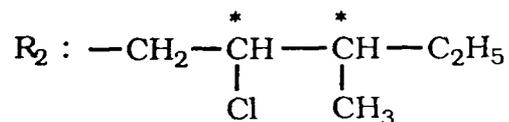
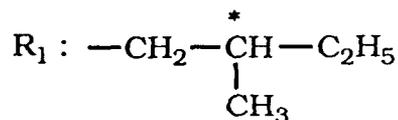
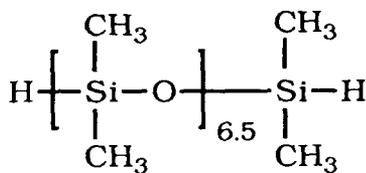
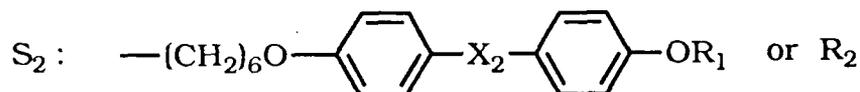
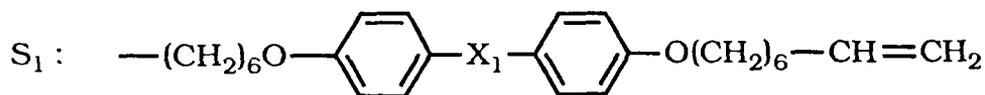
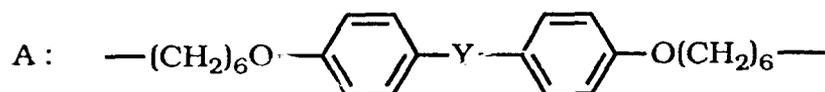


Crosslinked polymers (88)

Scheme 8. Synthesis of liquid crystalline elastomers **88** containing azo dyes by reaction of functionalized side chain liquid crystalline copolymers with 4,4'-diphenylmethane diisocyanate

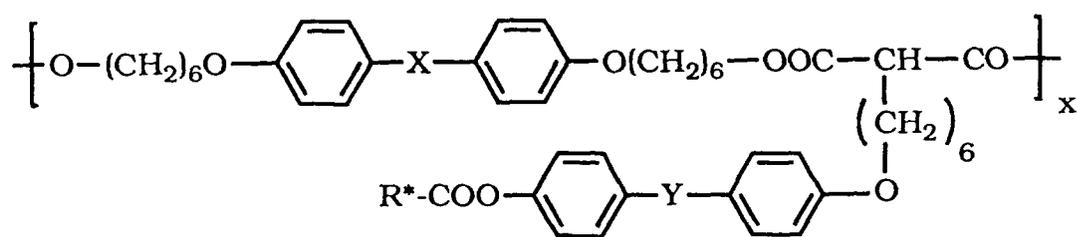


89a-91a



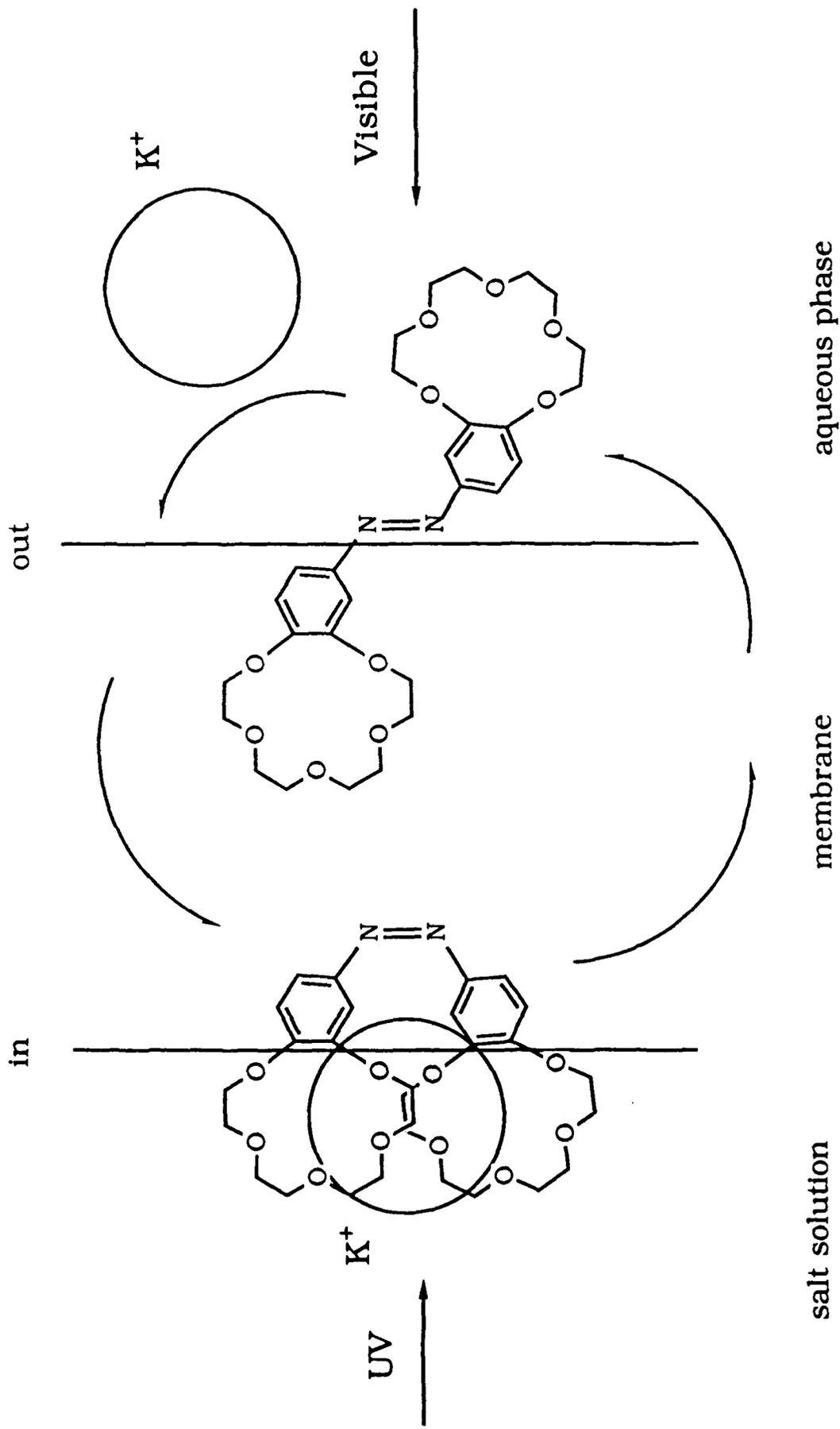
Crosslinked chiral elastomers (89b-91b)

Scheme 9. Synthesis of chiral liquid crystalline elastomers 89b-91b by hydrosilylation of vinyl functionalized liquid crystalline main chain/side chain combined polymers (89a-91a) with hydride terminated dimethylsiloxane oligomers

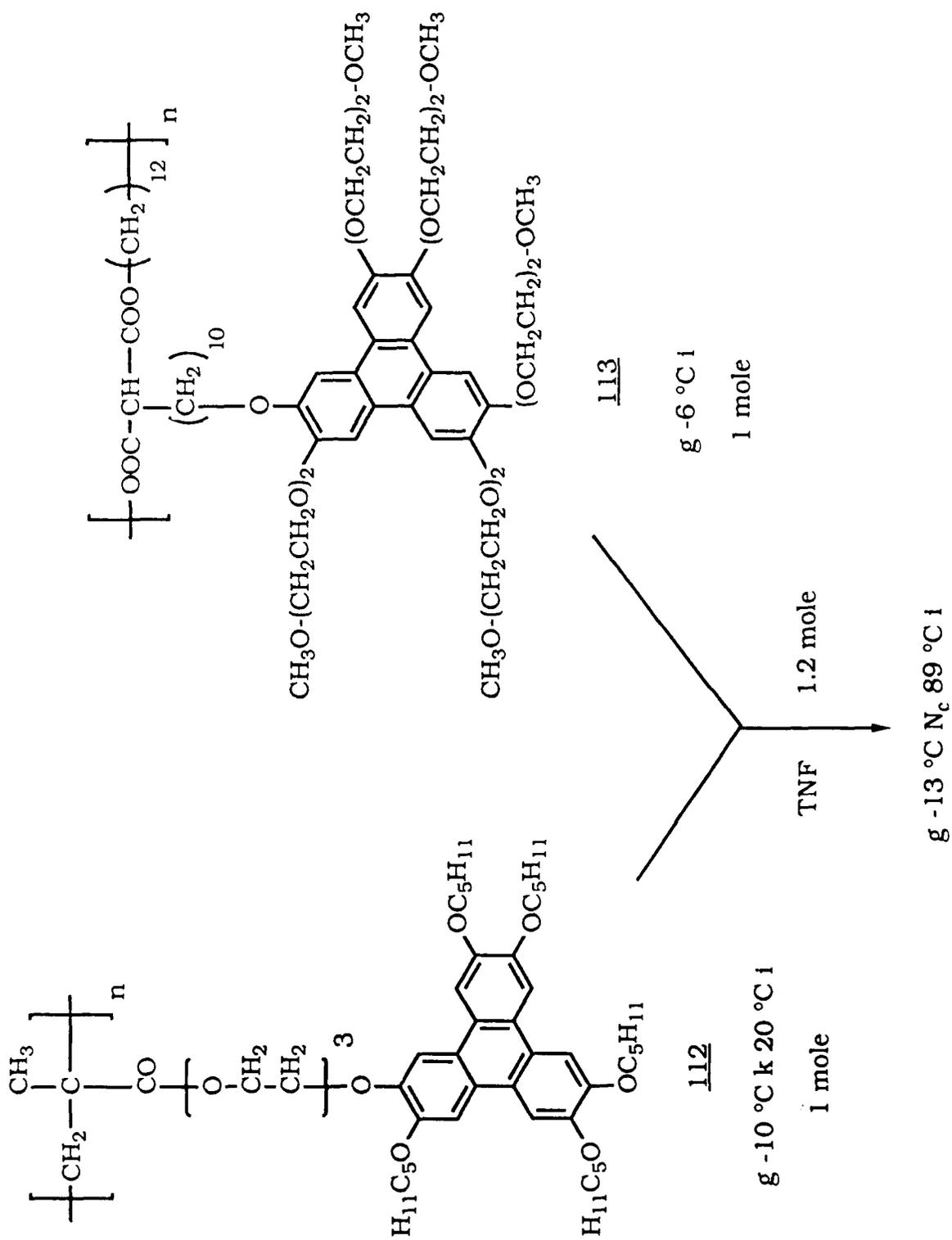


92-94

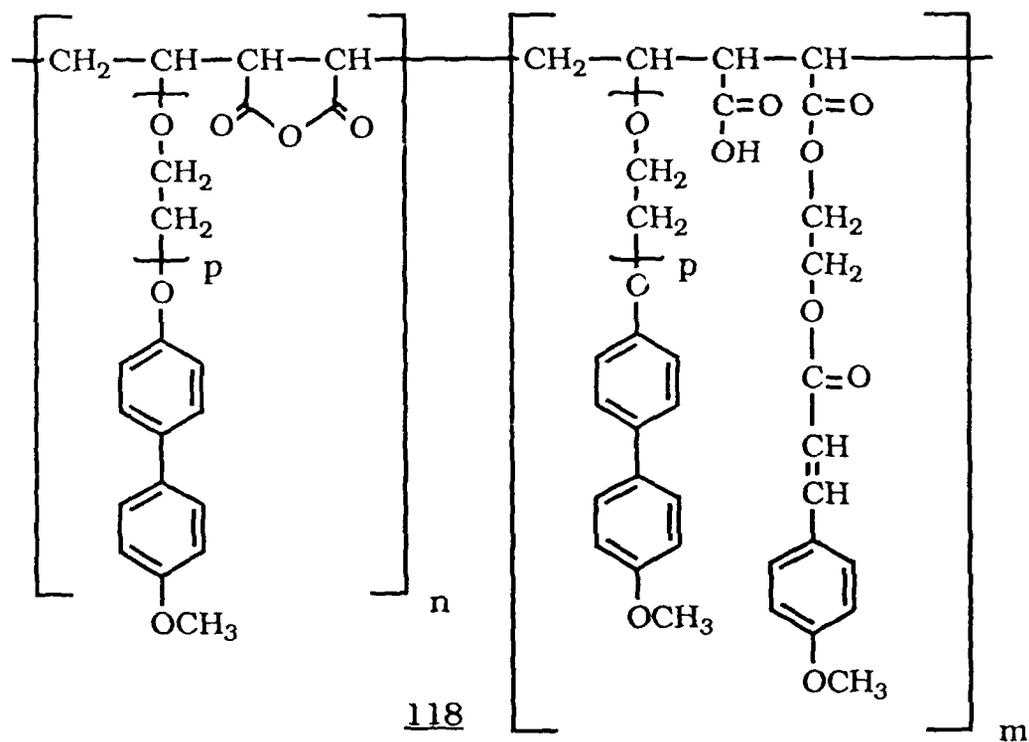
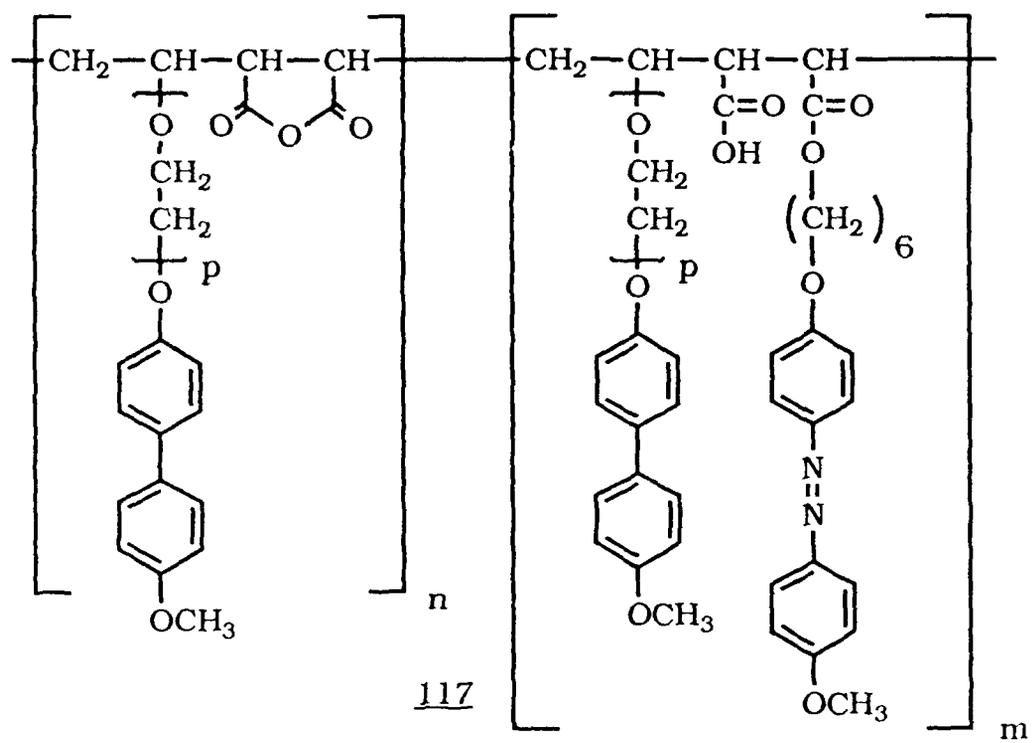
Scheme 10. Combined main chain/side chain chiral liquid crystalline homopolymers



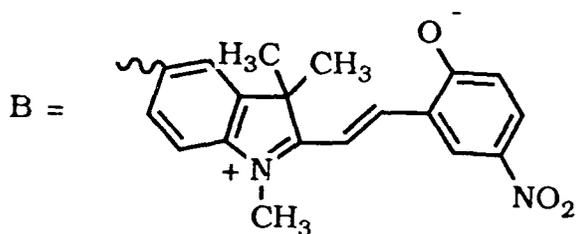
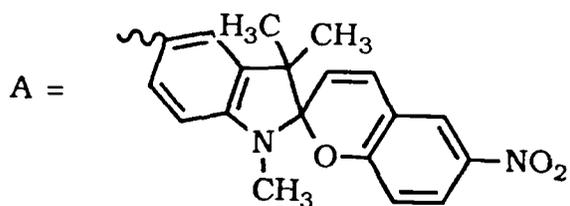
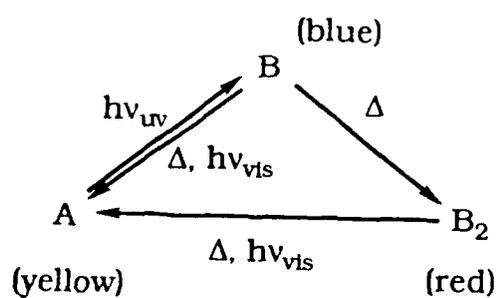
Scheme 12. Ion transportation mechanism in light-driven membrane composed of polyvinylchloride/low molar mass liquid crystal/azo bridged crown ether



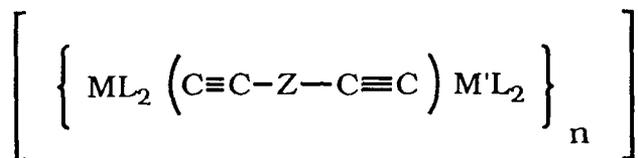
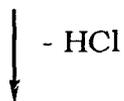
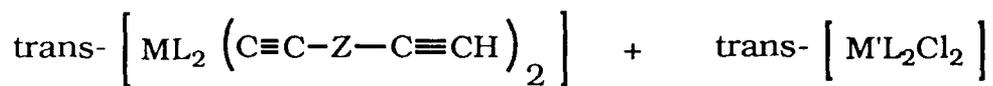
Scheme 13. Induction of compatibility and liquid crystallinity by doping of a blend of non-liquid crystalline polymers **112** and **113** with 2,4,7-trinitrofluorenone (TNF)



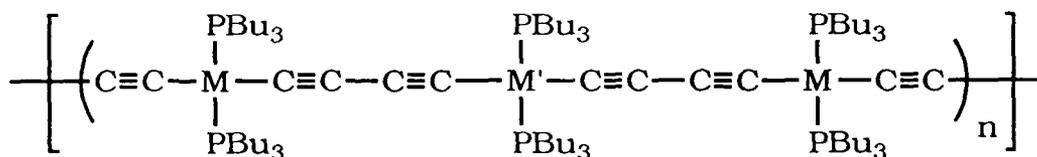
Scheme 14. Poly(biphenyl vinyl ether-alt-maleic anhydride)s containing azo (117) and cinnamate ester (118) moieties



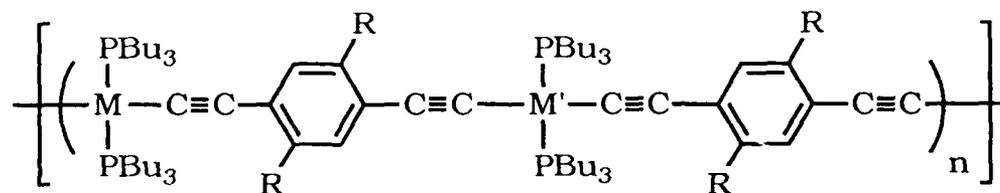
Scheme 15. Photochromic/thermochromic modulation of the interconversion of spiropyran (A) to merocyanine (B) and vice versa



134



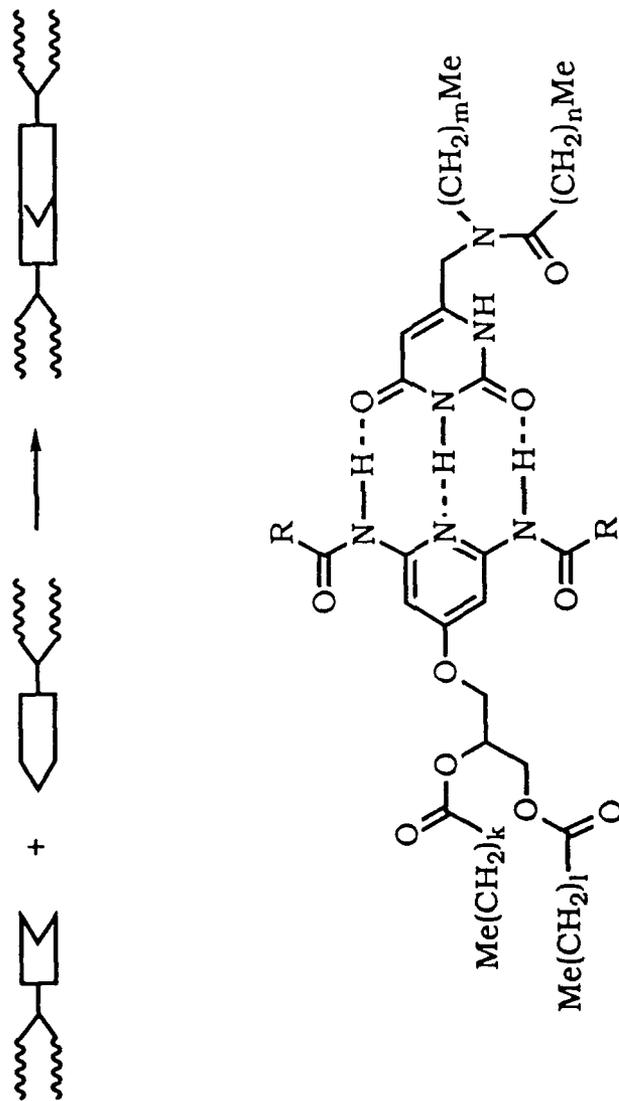
135



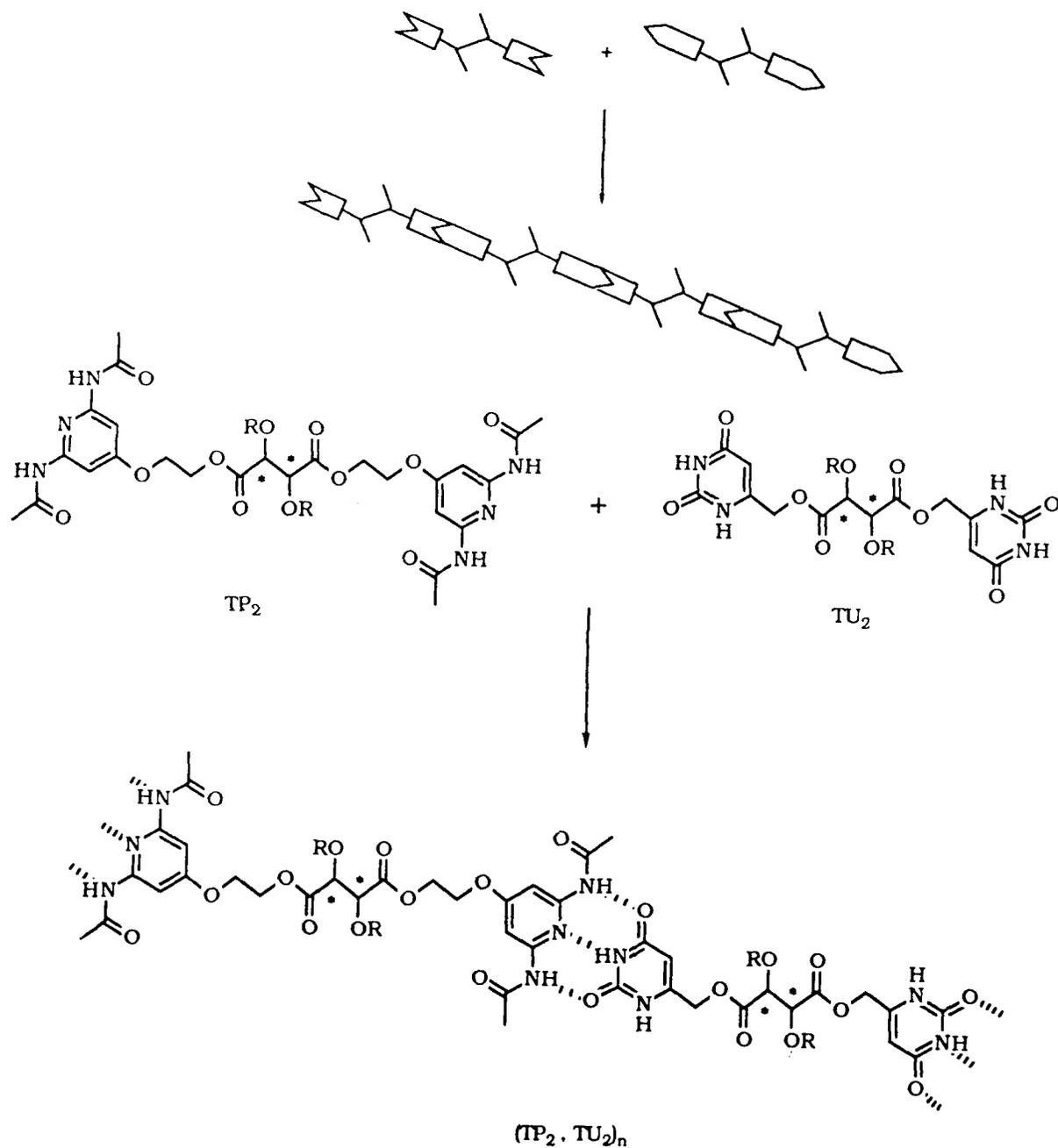
136

R = H, CH₃, C₂H₅

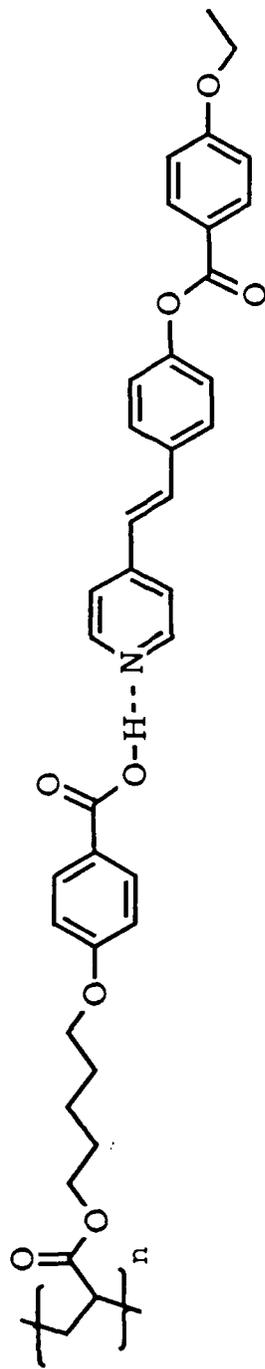
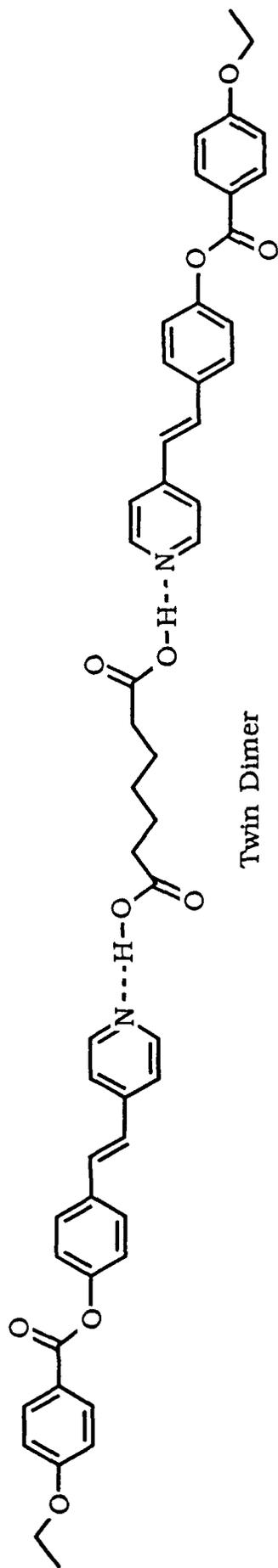
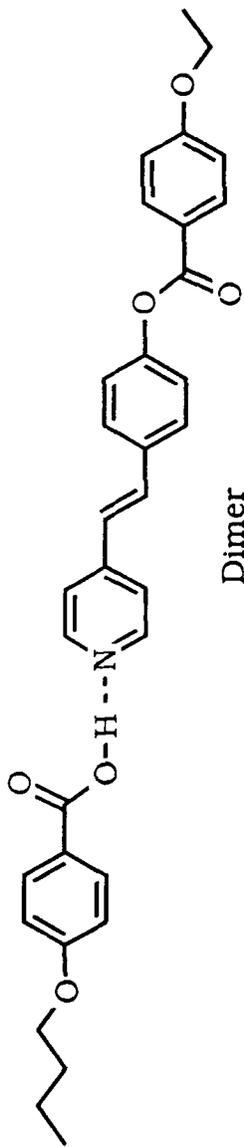
Scheme 16. Synthesis of liquid crystalline polyynes by coupling of metal halides and substituted alkynes



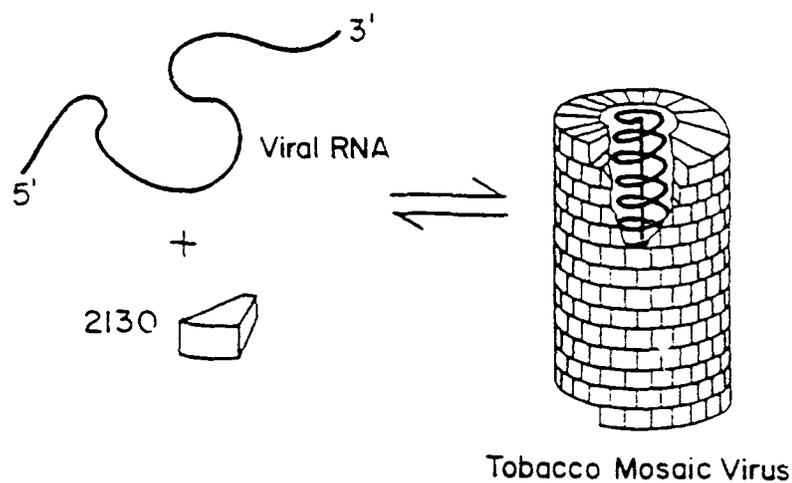
Scheme 17. Schematic representation of the formation of a supramolecular mesogen from two complementary components by an array of three parallel hydrogen bonds between their uracil and 2,6-diacylaminopyridine groups



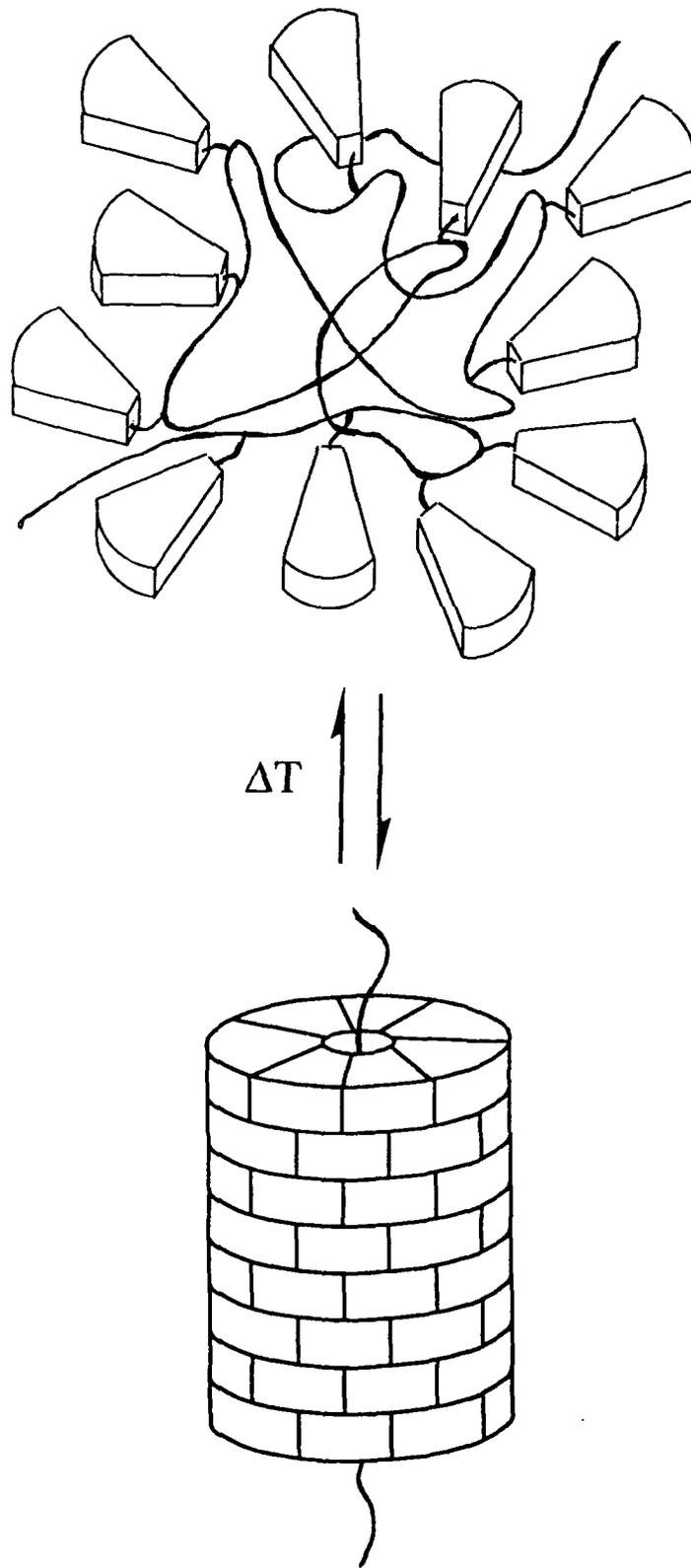
Scheme 18. Schematic representation of the formation of a supramolecular liquid crystalline polymer by the association of two complementary ditopic components based on uracil (U) and 2,6-diacetylaminopyridine (P) groups through the formation of three parallel hydrogen bonds



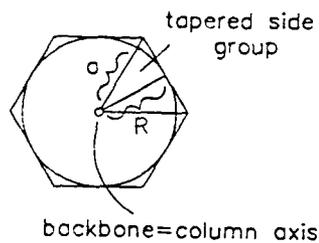
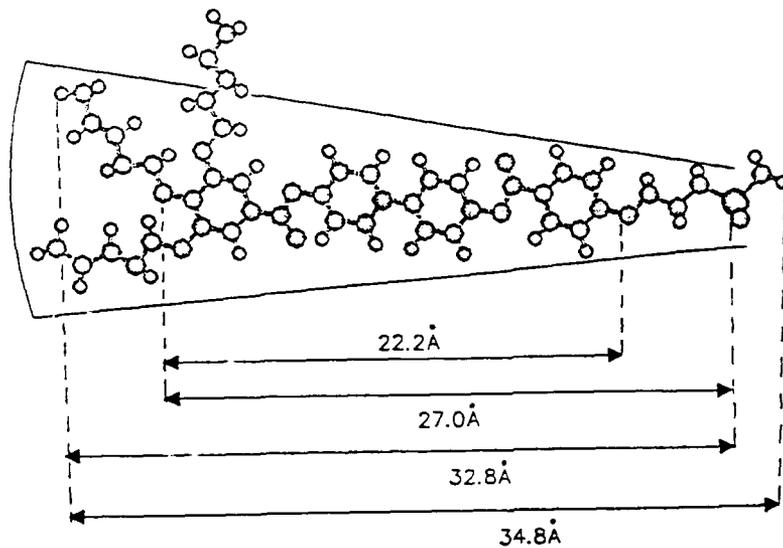
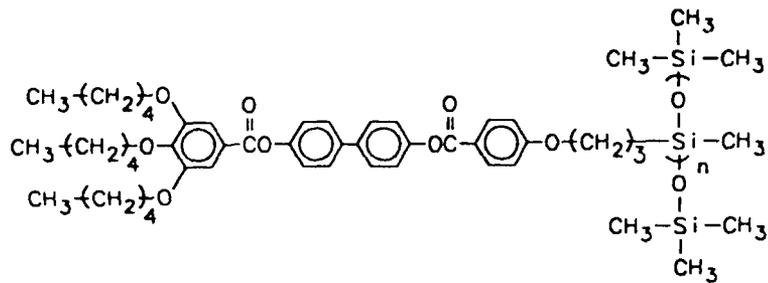
Scheme 19. Examples of nonsymmetric dimer, twin dimer and side chain liquid crystalline polymer generated by specific hydrogen bonding interactions



Scheme 20. Self-assembly of tobacco mosaic virus (TMV). The protein subunits define the shape of the helix and the RNA defines the helix length. All information for assembly is contained within the component parts. The structure contains $16 \frac{1}{3}$ protein subunits per turn and 2130 identical protein subunits (17,500 daltons each). The virus dimensions are 3000 Å in length, 180 Å in diameter, a helical pitch of 23 Å, a central hole of 40 Å, with 3 nucleotides bound per protein subunit



Scheme 21. The self-organization of a randomly coiled flexible polymer containing tapered side groups into a rigid rod-like columnar structure

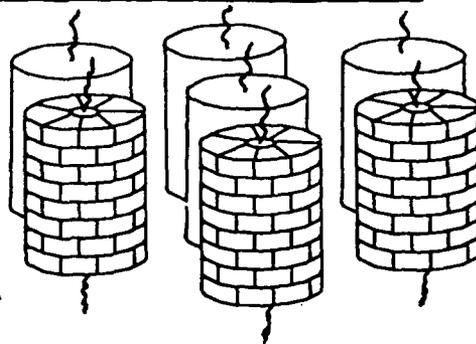


tail length=5 carbons
 $d_0=46.5\text{Å}(\text{strong})=d_{100}^{\text{hex}}$
 $d_1=26.5(\pm 0.5)\text{Å}(\text{weak})=d_{110}^{\text{hex}}$
 $d_1/d_0=1.75\approx\sqrt{3}$
 radius= $R=d_{100}/\sqrt{3}=27\text{Å}$
 diameter= $2R=54\text{Å}$
 $a=(2/\sqrt{3})R=31\text{Å}$

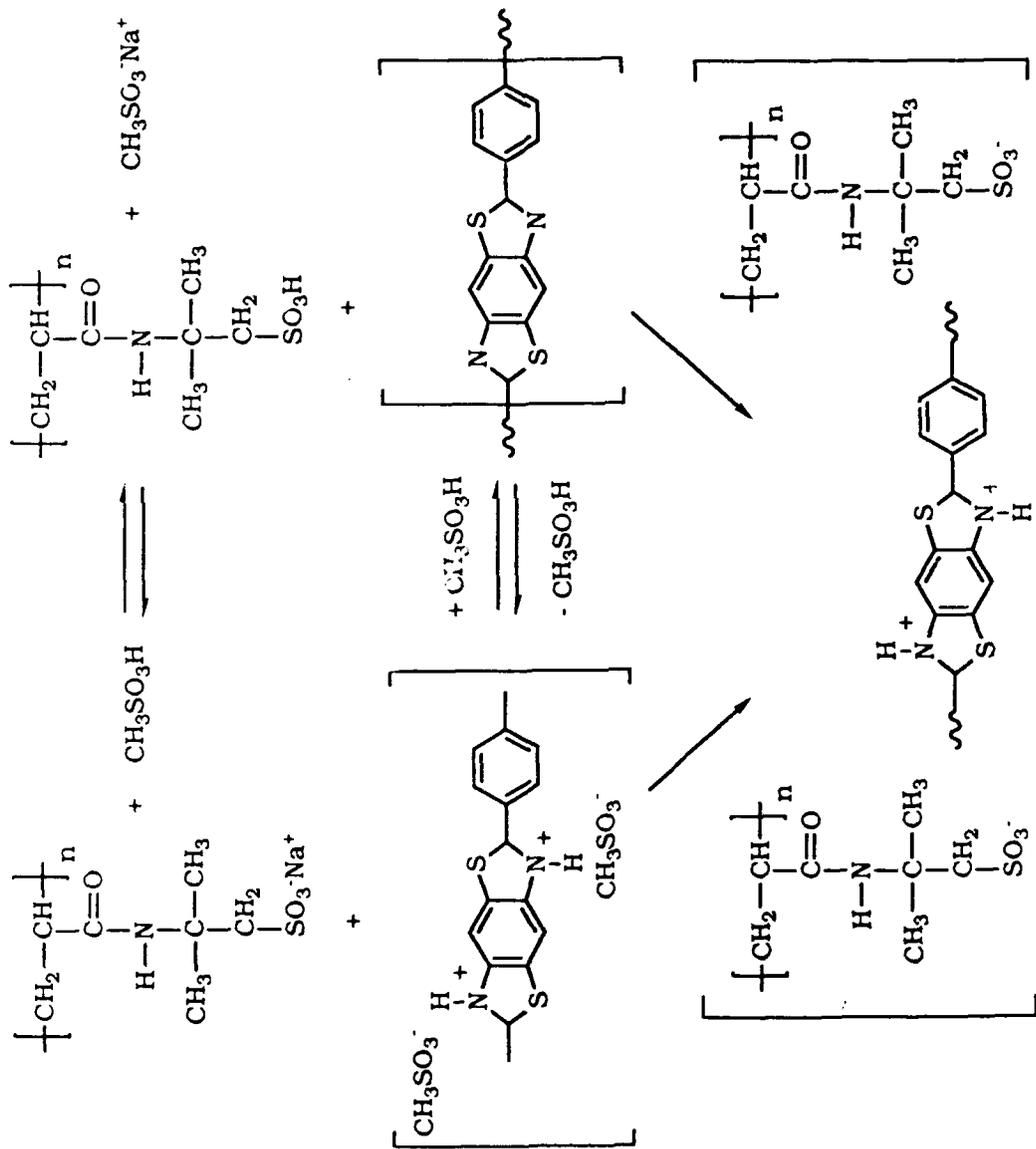
tail length=12 carbons

$d_0=57.4\text{Å}(\text{strong})=d_{100}^{\text{hex}}$
 $d_1=33.3\text{Å}(\text{v.weak})=d_{110}^{\text{hex}}$
 $d_2=28.5\text{Å}(\text{v.weak})=d_{200}^{\text{hex}}$

radius= $R=33.5\text{Å}$ diameter= $2R=67\text{Å}$
 fully extended conformation= 42Å

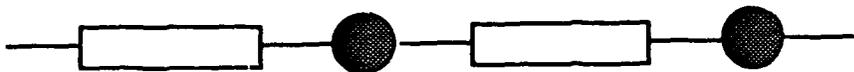


Scheme 22. A representative structure of a flexible polymer containing tapered side-groups and its self-assembling into a columnar structure which exhibits a hexagonal columnar mesophase



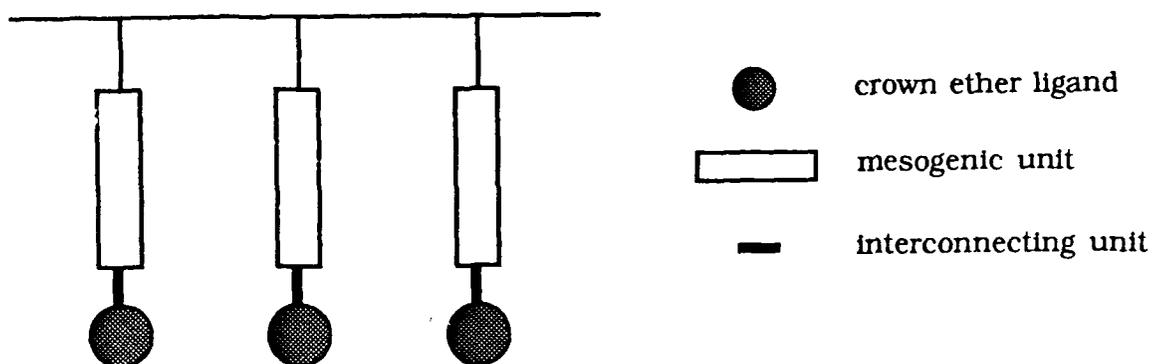
Scheme 23. Generation of a miscible polymer blend between the rigid rod-like poly(p-phenylene benzobisthiazole) and the flexible poly(sodium 2-acrylamido-2-methylpropane sulfonate) in methanesulfonic acid solution through ionic interactions

I. Main Chain Liquid Crystalline Polymers

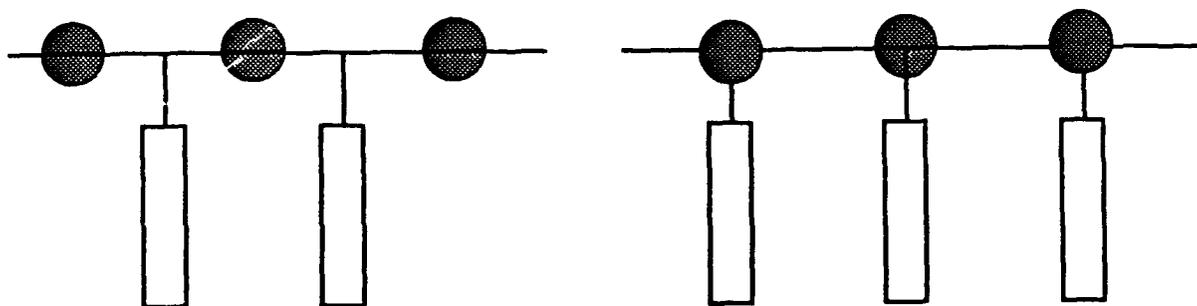


II. Side Chain Liquid Crystalline Polymers

A. Crown ether ligand as part of the mesogenic unit



B. Crown ether ligand as part of the polymer backbone



Scheme 24. The molecular architecture of liquid crystalline polymers containing crown ether ligands